

## **Analysis of Subsurface Metabolism in Groundwater Modeling**

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Citations in this document are numbered and listed in the literature cited. Footnotes are in lower case letters where additional information can be found at the bottom of the page.

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## Abbreviations, Nomenclature, and Glossary

ASM	Aerobic Soil Metabolism
1m0x, 2m0x, 3m0x, 4m0x	Modeling assumption where the first number indicates the assumed zone of aerobic soil metabolism (1, 2, 3, or 4-meter depth). The 0x indicates that a background degradation rate was not assumed, and the hydrolysis input reflected measured hydrolysis data.
1m10x, 2m10x, 3m10x, 4m10x	Modeling assumption where the first number indicates the assumed zone of aerobic soil metabolism (1, 2, 3, or 4-meters depth). The 10x indicates that a background degradation rate was assumed as 10x the aerobic soil metabolism half-life.
Breakthrough	The PWC defined breakthrough time in days as, “The average time that it takes to move a molecule of pesticide from the soil surface to the aquifer. It represents the average number of days that are required to leach one throughput.”
DWA	Drinking Water Assessment
EDWC	Estimated Drinking Water Concentration
EFED	Environmental Fate and Effects Division
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
GW	Groundwater
HED	Health Effects Division
Kd	Soil-water distribution coefficient in L/kg-soil
Koc	Organic-carbon normalized soil-water distribution coefficient in L/kg-organic carbon
NOM	Natural Organic Matter
OC	Organic Carbon
OCSPP	Office of Chemical Safety and Pollution Prevention
PBA	Post-breakthrough average
PRZM	Pesticide Root Zone Model
PWC	Pesticides in Water Calculator
Throughput	The PWC reports the number of throughputs that occur in a simulation which is “the estimated throughput (pore volumes/retardation factor) that occurred for the simulation. A throughput of one is required to expel the center of mass of Dirac pulse input. Near complete breakthrough will require several throughputs.
Vadose Zone	Also known as the unsaturated zone, is the soil between the land surface and the soil which is saturated with water. The unsaturated zone contains both soil, air, and water. Vadose is the Latin word for shallow.
USEPA	United States Environmental Protection Agency
WQP	Water Quality Portal

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## 1 Introduction

The Environmental Fate and Effects Division (EFED) provides estimates of exposure to pesticides in drinking water to the Health Effects Division (HED) for use in human dietary risk assessment. Drinking water exposure is estimated with the Pesticides in Water Calculator (PWC), which is used for both surface water and groundwater (GW) sources.

The Pesticide Root Zone Model Groundwater (PRZM-GW), now implemented in the PWC, was developed as a regulatory model to estimate pesticide concentrations in vulnerable groundwater sources as part of a North American Free Trade Agreement (NAFTA) and implemented in 2012[ ADDIN EN.CITE

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 title></titles><dates><year>2014</year></dates><urls></urls></record></Cite></EndNote>].  
 Hydrolysis is assumed to occur throughout the soil profile.

Since implementing PRZM-GW eight years ago it has become apparent that, on occasion, the  
 GW estimated drinking water concentrations (EDWCs) are orders of magnitude higher than  
 concentrations observed in monitoring data[ ADDIN EN.CITE ADDIN EN.CITE.DATA ]. Many  
 of these overestimates are for pesticides that do not hydrolyze and thus were assumed to be  
 stable below 1-meter. To address these overestimates, EFED scientists in collaboration with the  
 Office of Research and Development (ORD), were tasked with evaluating the available  
 information related to subsurface degradation and to revisit the groundwater conceptual  
 model. To support this, a literature search was completed and changes in standard modeling  
 assumptions were explored by comparing predicted pesticide concentrations, estimated using  
 alternative modeling assumptions, to measured concentrations. PWC modeling results were  
 compared to Office of Chemical Safety and Pollution Prevention (OCSPP) Guideline 835.7100  
 prospective groundwater (PGW) monitoring study[ ADDIN EN.CITE  
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0044</url></related-urls></urls><access-date>July 8, 2014</access-date></record></Cite></EndNote>] results. PGW studies are targeted monitoring studies with known pesticide usage that are designed to capture pesticide concentrations at sites vulnerable to contamination via leaching. The simulation was parameterized to match the application scenario employed in the PGW study (*i.e.*, 1-year of applications). Dissolved phase pesticide GW monitoring results obtained from the Water Quality Portal (WQP)<sup>a</sup> were also compared to the PWC predicted concentrations using different modeling assumptions.

The options explored for including subsurface metabolism in the PWC modeling are 1) to change the zone of ASM in the conceptual model or 2) to assume a background degradation rate throughout the soil profile. The following alternative modeling assumptions for simulating subsurface metabolic activity in the PWC model were explored:

- (1) increasing the depth at which metabolic activity in PWC declines to zero from 1-meter to a greater depth (2, 3, or 4-meters);
- (2) assuming the background degradation rate is 10 times the surface ASM input value for pesticides stable to hydrolysis, while holding the metabolism depth at 1-meter; and
- (3) items 1 and 2 combined.

**Section 3** of the document summarizes a literature review completed to understand metabolic activity of pesticides in the unsaturated zone of the subsurface, with emphasis on comparing measured half-life values in surface and subsurface soils collected from the same site. **Section 4** summarizes how the alternative modeling assumptions explored impact EDWCs. **Section 5** and **6** provide the details of the analyses of the options explored for including subsurface metabolism in the PWC modeling. **Section 7** summarizes the findings in this document.

## 2 Problem Formulation

Under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA; 7 USC § et seq. 1996) all pesticides distributed or sold in the United States must be registered with the USEPA. As part of this registration process, registrants submit a variety of physical-chemical and environmental-fate data to the EPA Office of Chemical Safety and Pollution Prevention (OCSP), Office of Pesticide Programs (OPP). These data include the rate of pesticide degradation (*i.e.*, half-life;  $T_{1/2}$ ) in surface soils, but do not include any subsurface degradation rates or aquifer/saturated zone rates.

The Environmental Fate and Effects Division (EFED) in the, U.S. EPA, is responsible for estimating exposure to pesticides in drinking water for human health risk assessment. Drinking

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<sup>a</sup> The Water Quality Portal a cooperative service sponsored by the United States Geological Survey (USGS), the Environmental Protection Agency, and the National Water Quality Monitoring Council (NWQMC). State, federal, tribal, and local agencies can submit water quality data into the database. Groundwater monitoring data available in the WQP have multiple objectives and are not specifically designed to evaluate the impacts of the use of pesticides in drinking water supplies. These groundwater monitoring studies may not be in vulnerable groundwater wells, often did not target use of pesticides, and may not all be drinking water sources.

water exposure is estimated by use of the Pesticides in Water Calculator (PWC), which provides estimates for drinking water from both surface water and GW sources. Drinking water estimates are provided to the Health Effects Division (HED) for use in the dietary risk assessment. Peak concentrations are used to evaluate the potential for acute toxicity, and post-breakthrough average concentrations are used to evaluate the potential for chronic or cancer toxicity endpoints to be exceeded.

## 2.1 Background on Groundwater Modeling

Since 2013[ ADDIN EN.CITE ADDIN EN.CITE.DATA ], EFED has been using a GW model (PWC, earlier Pesticide Root Zone Model in Ground Water (PRZM-GW)) after consultation with Science Advisory Panels[ ADDIN EN.CITE ADDIN EN.CITE.DATA ]. PWC makes it possible to simulate site specific exposure estimates with varying pesticide fate inputs, soil and aquifer properties, weather, and usage levels over multi-year periods. PWC-derived GW concentrations are most strongly influenced by the pesticide sorption coefficient, the aerobic surface soil metabolism rate, and the hydrolysis rate. The hydrolysis rate is especially important for the way PWC estimates transformation of the pesticide when considering subsurface metabolism because the current conceptual model assumes that only hydrolysis occurs below 1 meter.

[ REF\_Ref34665143 \h \\* MERGEFORMAT ] 2-1 depicts the general GW scenario concept for estimating pesticide concentrations in drinking water. The conceptualization of this GW scenario evolved from meetings between North American Free Trade Agreement (NAFTA) partners EPA and the Pesticide Management Regulatory Authority (PMRA) and from the 2005 N-Methyl Carbamate Science Advisory Panel (SAP) meetings[ ADDIN EN.CITE <EndNote><Cite><Author>USEPA</Author><Year>2005</Year><RecNum>5301</RecNum><DisplayText><style face="superscript">10, 11</style></DisplayText><record><rec-number>5301</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184598" guid="ddc2d036-bc5b-4c33-9984-7e7723579651">5301</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>USEPA</author></authors><secondary-authors><author>EPA Docket Number EPA-HQ-OPP-2005-0172</author></secondary-authors></contributors><titles><title>Federal Insecticide, Fungicide, and Rodenticide, Act (FIFRA) Scientific Advisory Panel: Preliminary N-methyl Carbamate Cumulative Risk Assessment</title><secondary-title>August 23-26, 2005</secondary-title><tertiary-title>Office of Pesticide Programs. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2005</year></dates><urls><related-urls><url>https://www.regulations.gov/document?D=EPA-HQ-OPP-2005-0172-0041</url></related-urls></urls></record></Cite><Cite><Author>USEPA</Author><Year>2005</Year><RecNum>5300</RecNum><record><rec-number>5300</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184598" guid="c02b761c-727b-436e-98e4-16035b0b1ebb">5300</key></foreign-keys><ref-type name="EPA Document">51</ref-

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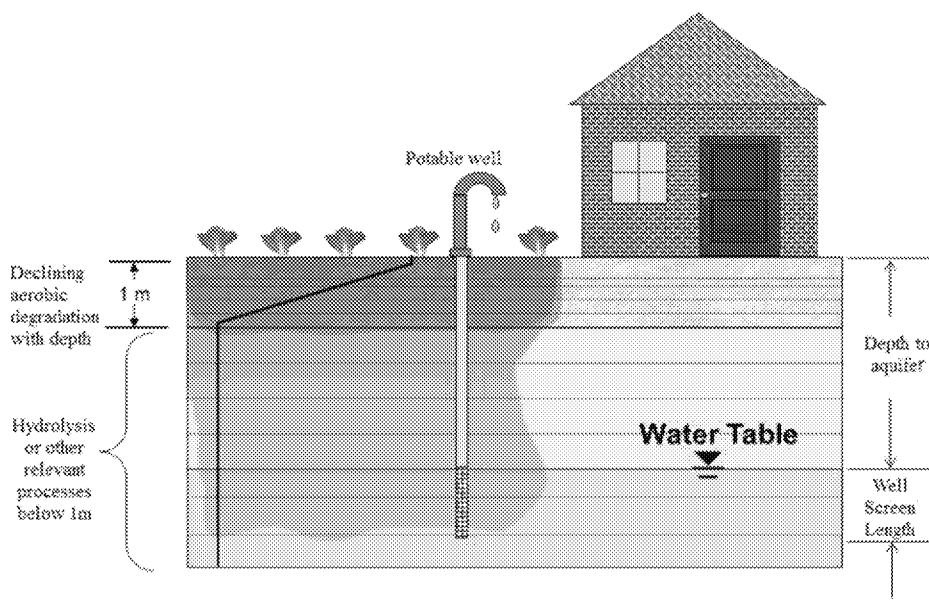


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. General Groundwater Conceptual Model

The conceptual model used in PWC is based on a drinking water well beneath an agricultural field (a high pesticide usage area), which draws water from an unconfined, high water-table aquifer. The depth of the well is site-specific (*i.e.*, scenario specific). The well extends into a shallow unconfined aquifer and has a well-screen that starts at the top and continues down into the aquifer. The length of the well-screen represents the region of the aquifer where drinking water is collected. The well-screen length is well-specific and can be adjusted. Processes included in the conceptual model include vertical water flow, solute advection and dispersion, chemical degradation, sorption, and crop specific factors, including evapotranspiration, pesticide interception and management practices.

The conceptual model of pesticide transport into the aquifer includes those process that were likely to have the greatest impact on estimating pesticide concentrations in the aquifer—such as water flow, pesticide degradation, and sorption. The conceptual model does not account for lateral flow and dispersion away from the treated site. See the full documentation[ ADDIN EN.CITE ADDIN EN.CITE.DATA ] of the conceptual model for more details on water flow, crop and management practices and other factors simulated in the model. This document focuses on degradation routine assumptions in the conceptual model.

Compounds moving through the soil profile can be slowed if they sorb onto soil particles or diffuse into soil organic matter. The basic conceptual model allows for linear instantaneous sorption, based on a soil-water distribution coefficient,  $K_d$ , defined as the ratio of the sorbed concentration (mass pesticide/mass soil) to soil solution concentration. For many pesticides, sorption occurs mainly on the soil organic matter, so for cases where  $K_d$  correlates with the soil organic matter content, an organic-carbon normalized soil-water distribution coefficient ( $K_{oc}$ ) can be used instead.

EFED currently has standardized the use of six geographically distinct GW scenarios for the PWC that represent areas vulnerable to contaminant leaching. The scenarios assume permeable soils and shallow unconfined aquifers in Florida, Georgia, North Carolina, the Delmarva (Delaware-Maryland-Virginia) peninsula<sup>b</sup>, and Wisconsin. These scenarios represent specific locations with soil, aquifer, and climatic characteristics such that some of the highest GW exposure potential of US agricultural areas is expected.

The rate of decay of a pesticide in the PWC model is selected based on the results of two laboratory experiments: the OCSPP ASM guideline 835.4100[ ADDIN EN.CITE <EndNote><Cite><Author>USEPA</Author><Year>2008</Year><RecNum>734</RecNum><DisplayText><style face="superscript">12</style></DisplayText><record><rec-number>734</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1337278484" guid="c76ed6af-3255-4c69-b897-e4086f05bc73">734</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>USEPA</author></authors><secondary-authors><author>EPA 712-C-08-016,</author><author>EPA 712-C-08-017,</author></secondary-authors></contributors><titles><title>OPPTS 835.4100 Aerobic Soil Metabolism; OPPTS 835.4200 Anaerobic Soil Metabolism</title><secondary-title>October 2008</secondary-title><tertiary-title>Office of Prevention, Pesticides, and Toxic Substances. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2008</year></dates><publisher>Fate, Transport, and Transformation Guidelines</publisher><label>Guideline</label><urls><related-urls><url>http://www.epa.gov/ocspp/pubs/frs/publications/Test\_Guidelines/series835.htm</url></related-urls></urls><access-date>August 22, 2014</access-date></record></Cite></EndNote>] and the OCSPP hydrolysis guideline 835.2120[ ADDIN

<sup>b</sup> A large peninsula on the Eastern Coast of the United States occupied by Delaware and parts of Maryland and Virginia.

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<EndNote><Cite><Author>USEPA</Author><Year>2008</Year><RecNum>718</RecNum><DisplayText><style face="superscript">13</style></DisplayText><record><rec-number>718</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1336409853" guid="355e333e-a85c-4330-b244-da580ae0d0e0">718</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>USEPA</author></authors><secondary-authors><author>EPA 712-C-08-012,</author></secondary-authors></contributors><titles><title>OPPTS 835.2120 Hydrolysis</title><secondary-title>October 2008</secondary-title><tertiary-title>Office of Prevention, Pesticides, and Toxic Substances. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2008</year></dates><publisher>Fate, Transport, and Transformation Guidelines</publisher><urls><related-urls><url>http://www.epa.gov/ocspp/pubs/frs/publications/Test\_Guidelines/series835.htm</url></related-urls></urls><access-date>May 5, 2012</access-date></record></Cite></EndNote>]. These degradation rates are adjusted by temperature, which varies with depth. In the top 1-meter, the ASM rate at the surface is equivalent to the input value and is assumed to decline to zero at 1-meter. The ASM rate is applied to both dissolved and sorbed pesticide. As both hydrolysis and ASM may occur in the dissolved phase, in the top 1-meter, degradation in the dissolved phase is set to either the hydrolysis rate or the ASM rate, whichever is faster. Below 1-meter degradation is assumed to only occur in the dissolved phase based on the hydrolysis input.

The assumption that ASM declines linearly to zero at 1-meter was made based on precedent of use in other GW models[ ADDIN EN.CITE

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title></titles><dates><year>2014</year></dates><urls></urls></record></Cite></EndNote>  
and based upon the best scientific judgment of the development team for PRZM-GW.

PWC GW modeling produces daily concentrations of pesticides in GW for the duration of the simulation. When estimating concentrations in GW, the simulation is initially run for 30-years. When throughputs are less than one (an indication that the estimated GW concentrations have not stabilized near their maximum level in the 30 years modeled), the simulation is, by rule in the Agency's guidance for the regulatory use of the model, extended to 100-years. Once throughputs are greater than one, the concentrations in GW will remain relatively constant. When throughputs are less than one, concentrations will continue to increase over time.

One *throughput*<sup>c</sup> is equivalent to the amount of water volumes in the vadose (unsaturated) zone that must be flushed through to move the center of mass of the contaminant plume into the aquifer. *Breakthrough* is defined in the PWC as occurring at one throughput. It is the average time (*e.g.*, days) that it takes to move a molecule of pesticide from the soil surface to the aquifer. The PWC calculates breakthrough from the average number of days that are required to leach one throughput. (The average is necessary because yearly rainfall varies from year to year and thus breakthrough will vary from year to year). [ REF \_Ref45444914 \h \\* MERGEFORMAT ] illustrates a PWC GW simulation with a single application in 1960. The breakthrough time is 3,606 days, about 10-years (November 1969 shown by the red line), and the throughputs are 3.04. These two numbers always multiply to the total number of days in the simulation (3,606 x 3.04 = 10,962 days or about 30 years); this is because breakthrough is defined in the PWC as occurring at one throughput.

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<sup>c</sup> The PWC reports the number of throughputs that occur in a simulation which is "the estimated throughput (pore volumes/retardation factor) that occurred for the simulation. A throughput of one is required to expel the center of mass of Dirac pulse input. Near complete breakthrough will require several throughputs.

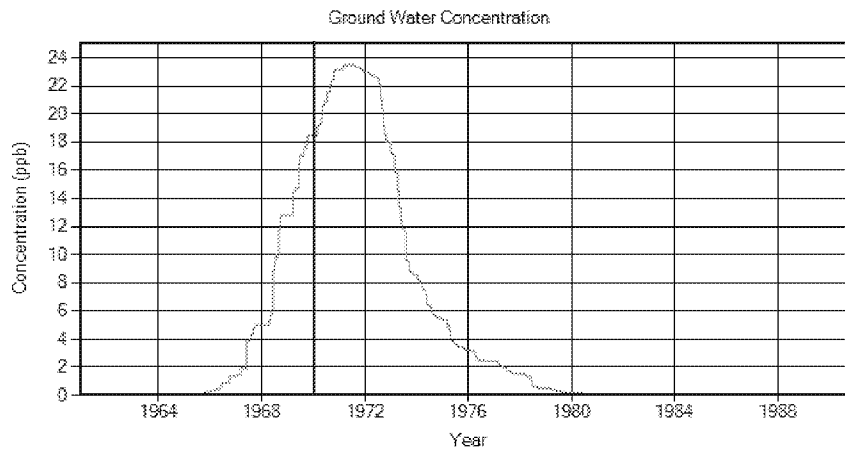


Figure [ STYLEREFF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Illustration of Breakthrough Time (Shown by the Red Line) as Defined by the PWC

For a perfect Dirac input and constant leaching, breakthrough would occur at the peak of the pulse, but because breakthrough time is an average over all years of an actual simulation, actual breakthrough does not necessarily occur at the peak of any particular pulse, as typical in the above graph.

The PWC estimates a peak, post-breakthrough average, and simulation average concentration. These are defined below:

- **Peak value:** This number is the highest simulated vertical-averaged concentration in the top 1 meter of the simulated aquifer. This is used to estimate dietary exposure for acute toxicity endpoints.
- **Post Breakthrough Average (PBA):** This number is the temporal average over the simulation period after one throughput has occurred. It represents the approximate dynamic steady state average of the vertical-averaged concentration (ppb) in the top 1 meter of the simulated aquifer. This exposure estimate is used to estimate dietary exposure for chronic and cancer toxicity endpoints.
- **Simulation Average value:** This number is the temporal average over the entire simulation period of the vertical-averaged concentration (ppb) in the top 1 meter of the simulated aquifer.

## 2.2 Analysis Plan

Since implementing PRZM-GW eight years ago it has become apparent that, on occasion, the GW estimated drinking water concentrations (EDWCs) are orders of magnitude higher than concentrations observed in groundwater monitoring data[ ADDIN EN.CITE <EndNote><Cite><Author>USEPA</Author><Year>2012</Year><RecNum>5244</RecNum><DisplayText><style face="superscript">1, 9</style></DisplayText><record><rec-



number>5244</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1535036560" guid="5462a21c-9e46-4eb3-bef7-2381d1408413">5244</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>USEPA,</author><author>Health Canada,</author></authors></contributors><titles><title>Identification and Evaluation of Existing Models for Estimating Environmental Pesticide Transport to Groundwater</title><secondary-title>October 15, 2012</secondary-title><tertiary-title>Environmental Fate and Effects Division. Office of Pesticide Programs. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2012</year></dates><urls></urls></record></Cite><Cite><Author>USEPA</Author><Year>2015</Year><RecNum>5299</RecNum><record><rec-number>5299</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184598" guid="fc527971-c2e5-4470-a5dd-81895cb06ae1">5299</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>USEPA</author></authors></contributors><titles><title>Use of PRZM-GW for Estimating Pesticide Concentrations in Tier 1 and Tier 2 Drinking Water Assessments</title><secondary-title>September 30, 2015</secondary-title><tertiary-title>Environmental Fate and Effects Division. Office of Pesticide Programs. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2015</year></dates><urls></urls></record></Cite></EndNote>]. Many of these overestimates are for pesticides that are persistent to hydrolysis and were assumed to be stable below 1-meter. EFED scientists in collaboration with ORD, were tasked with evaluating the available information related to subsurface degradation and to revisit the previous conceptual model for estimating residues in groundwater.

When considering how to approach this issue, it is important to understand that surface and subsurface metabolism rates of pesticides in soils are influenced by a number of different factors and can vary by as much as 80x across soils for one pesticide[ ADDIN EN.CITE ADDIN EN.CITE.DATA ]. Pesticide degradation is a complex issue as there is 1) not a set of dominant controlling variables for subsurface pesticide degradation across all pesticides and soils, 2) there is a high degree of variation among pesticide chemical species, and 3) there are a large number of environmental variables that often vary over orders of magnitude between locations. For example, pesticides degrade by a variety of abiotic and enzyme-mediated mechanisms, *e.g.*, neutral hydrolysis, pH-dependent hydrolysis, reduction, oxidation, and potentially by multiple mechanisms simultaneously at different reaction centers. Adding to the complexity, environmental systems constitute many interacting variables that rarely are adequately defined to allow extrapolation to other settings. Environmental variables that might affect degradation of one or more pesticides include, pH, redox conditions, mineralogy, organic carbon concentration, and several other variables.

Up to now refinements utilized in drinking water assessments focused on using alternative model inputs and not changing the conceptual model. For example, using a less conservative ASM input based on results from a terrestrial field dissipation study, or obtaining more refined

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hydrolysis data from the literature, etc. Based on available guidance, additional data on subsurface metabolism would be needed in order to assume that degradation other than hydrolysis occurred below 1-meter. For this work, EFED focused on using available data and alternative assumptions, so that refinements in GW modeling could be made without obtaining additional data.

The first step in this effort was to complete a literature search for data on subsurface metabolism. EFED and ORD searched open literature data for studies that measured degradation rates at the surface and subsurface in the same soil and especially for studies that evaluated subsurface degradation at depths greater than 1-meter.

The second step of this work involved exploring the two options for refining the subsurface metabolism assumptions (increasing the zone of metabolism or assuming a background degradation rate throughout the soil profile) and comparing the resulting modeled pesticide concentrations in GW to monitoring result. The modeling and monitoring comparison may be used to evaluate whether implementing the refinements could be considered reasonable and protective of potential exposure in GW. Pesticide occurrence data (*i.e.*, measured concentrations) from PGW monitoring studies and from the Water Quality Portal were considered.

#### 2.2.1 Options Considered for Subsurface Modeling

We considered two basic options 1) modification of the model regarding subsurface assumptions and 2) changes in the input parameter guidance. The two options were considered because these are the two items that can be altered to account for degradation in the subsurface. The first option involves increasing the zone of ASM assumed in the model, which will increase the depth in which ASM is simulated by the model, and still accounts for the general assumption that ASM will be slower in the subsurface than at the surface.

As the model is currently set up to simulate hydrolysis through the entire soil profile, this input can be utilized in understanding subsurface degradation. Essentially, the hydrolysis is assumed to represent a background degradation rate for the dissolved phase throughout the soil profile. Data are available to support that there is microbial activity in the subsurface for some soils and for some chemicals; however, it usually occurs at a lower rate than at the surface. Therefore, any background rate must be lower than what occurred in the surface. We explored making the background degradation rate be based on the surface ASM for the second option. Here the subsurface half-life is set based on what is predicted to occur at the surface (multiplied by a factor to account for the rate being lower than what will occur at the surface). This assumption only applies to chemicals that are stable to hydrolysis or where the hydrolysis half-life would be slower than the assumption for the background degradation rate. For all pesticides analyzed that did undergo hydrolysis, the measured hydrolysis half-life was faster than the background degradation rate assumption. Therefore, this assumption is mainly applicable to pesticides stable to hydrolysis.

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When considering whether to move forward with either option it should be considered (1) whether data support the assumption and (2) whether the results predict concentrations that more closely align with measured values and are still protective of potential exposure in drinking water. Finally, both approaches can be considered one way to calibrate the model to be both reasonable and conservative by comparing PWC estimated concentrations to pesticide occurrence data (especially prospective groundwater monitoring results).

The data quality objectives of the evaluation of the subsurface modeling assumptions is to minimize over and underprediction of the majority of pesticides, especially those that are a major concern for GW contamination (*i.e.*, mobile and persistent pesticides). This fulfills the need for the model to be reasonable in predicting potential concentrations in GW. For the model to be conservative, it is generally desired that modeled/predicted concentrations will be higher than measured concentrations but not by a large amount. Two ways to balance being both reasonable and conservative is:

- 1) to allow for some predicted concentrations to underpredict measured concentration but minimizing the magnitude of that underprediction and for how many cases this occurs; and
- 2) to focus on being protective of pesticides known to have GW exposure issues.

The number of pesticides where modeled concentrations are lower than measured concentration should be minimized.

### 2.3 Overview of Analysis/Sections

The remainder of this document is organized into four sections. **Section 3** discusses the review and analyses completed for open literature studies related to subsurface metabolism.

**Section [ REF\_Ref36455487 \r \h ]** explores how modeling results change when implementing changes in subsurface modeling assumptions. The modifications considered are:

- (a) an increase in the metabolism depth from 1-meter to 2, 3, or 4 meters (up to the depth of the water table);
- (b) assuming a background degradation half-life of with 10x or 25x the ASM, for pesticides stable to hydrolysis; and
- (c) combinations of (a) and (b).

The effect of the model assumption changes on both peak concentration and post-breakthrough average concentration (used for acute and chronic exposure estimation, respectively) are presented. While a range of assumptions for increasing the zone of metabolism were explored (up to 4-meters), much of the analysis focused more heavily on the results considering a 2-meter zone of metabolism because very limited data are available examining subsurface metabolism below 2-meters.

**Section [ REF\_Ref36455536 \r \h ]** presents a comparison of the two main model modification options under consideration, to the results of PGW studies. The comparisons are for the specific pesticides tested in the PGW study, to PWC model runs for a PWC scenario most closely matching the place where the PGW study was conducted. Comparisons were made to

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determine if the modeled EDWCs were more like the observed values in the PGW studies, while remaining conservative.

**Section [ REF \_Ref36382537 \r \h ]** presents an analysis of GW monitoring data obtained from the WQP to the results of our PWC modeling. This helped us to determine whether the proposed modeling changes were appropriate for pesticides with a broader range of pesticide properties including some that were considered *a priori* to pose less of a GW contamination threat (and would typically not be examined in PGW studies).

**Section [ REF \_Ref36455936 \r \h ]** summarizes the results.

The Appendices include supporting materials and not all of the materials are discussed within the body of the document. The Appendices are as follows:

[ TOC \h \z \c "Appendix" ]

### 3 Open Literature Analysis

We collected data from the open literature to better understand the state of the science of subsurface metabolism of pesticides. The objective of the literature review was to gather information on rates of metabolism of pesticides in the subsurface to compare how modeling assumptions compared with subsurface metabolism data.

#### 3.1 Data Collection Methods

One approach to better understanding subsurface metabolism is to compare rates of transformation in a surface soil to the rate of transformation in a subsurface soil collected at the same site (*i.e.*, paired soil samples). Use of paired surface- and subsurface-soils circumvent uncertainties associated with the myriad of factors affecting degradation rates by using identical pesticides and laboratory methods within each study to generate both the surface and subsurface transformation rates. These paired soils reflect real-world variability that is present at single locations between surface and subsurface soils in terms of mineralogy, particle size, organic carbon concentration and composition, pH and other factors affecting degradation rates. Most of these soil degradation experiments were conducted in the lab. Had the soils been tested in the field, rates might have been different, e.g., longer half lives.

Members of the workgroup searched for peer-reviewed papers (primary sources) where transformation rates were measured in soils collected at the surface, and at a defined subsurface depth. The studies were for aerobic systems and could reflect a laboratory or field study. Soils were collected from an unsaturated zone and soils were characterized. Information on soil texture, percent organic-carbon, pH, and Kd were collected when available.

Studies with the following characteristics were not included:

- data where volatilization or dissipation may have influenced the results;

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- data where only degradation percent was reported; and
- mineralization<sup>d</sup> rates.

These studies were from peer-reviewed scientific journals but did not necessarily have raw data available or information regarding the mass balance of applied material. However, methods and results were deemed to be clear, transparent, and reliable using best professional judgement.

The Web of Science Database was searched<sup>e</sup> using either “vadose zone” or “groundwater”, and one additional keyword from this list: aerobic, anaerobic, aquifer (years restricted to 2014-2016), carbon dioxide, contamination, flow (years restricted to 2014-2016), heterogen\*, microbial, model (years restricted to 2014-2016), moisture, nutrient, organic matter, oxygen, pesticide, review, sediment, software, temperature, and transport. Search results were collected in an Endnote database consisting of >25,000 publications. Then this Endnote database was searched by keywords including individual pesticide names and related terms.

All paired studies[ ADDIN EN.CITE ADDIN EN.CITE.DATA ADDIN EN.CITE.DATA ] were tabulated in an Excel spreadsheet along with depths from which the subsurface sample was drawn as well as any additional potentially useful ancillary data that were reported in the studies. In this database, transformation data were recorded as half-lives, DT<sub>50</sub>, or as rates. When converting between rate constants and half-lives, these values were converted according to a single-first order (SFO) assumption:

$$T_{1/2} = \ln 2 / k \quad (1)$$

where T<sub>1/2</sub> is the half-life in days, and k is the first-order rate constant (day<sup>-1</sup>). Most data were reported as SFO values (see **Appendix A**). Ancillary data included in this tabulation varied between studies and was limited to that reported in the original study, but commonly included pH, organic carbon concentration and unsaturated vs saturated subsurface conditions.

With a few variations, a similar search was conducted to see if additional data could be found for pesticides with a wider range of properties including pesticides that were more persistent, historically had GW contamination concerns, or were previously considered in the development of the GW modeling in OPP. Each search was initiated with the chemical name and then refined considering the following key words: “soil”, “vadose subsurface or subsoil or aquifer or GW or leaching” and “half-life”. No date restrictions were made for these searches. Following the review of these studies for inclusion of paired surface- and subsurface-soil pesticide transformation rates (or half-lives), any additional literature was also included in the

<sup>d</sup> Mineralization is based on formation of carbon dioxide. While the mineralization rate can provide useful information in understanding degradation and transformation in the subsurface, the rate of metabolism of the pesticide is not the same as the rate of mineralization due to the formation of intermediate degradates.

<sup>e</sup> This initial search was completed by the Office of Research and Development (ORD).

spreadsheet. Further review and inclusion of data by EFED resulted in a total of 159 paired surface- and subsurface-transformation data.

A comparison was made between the open literature surface ASM half-life values and ASM half-life values from studies that were conducted according to the OCSPP guideline on ASM. Half-lives for hydrolysis and ASM were obtained from EFED drinking water and ecological assessments. These results are summarized in **Appendix C**.

### 3.2 Data Assessment

Data across 39 chemicals are available and summarized in **Appendix A**. Most of the measured half-life values were below 200-days<sup>f</sup>. Soil samples were collected at various depths in each study down to 17 m, with most samples collected at depths shallower than 1-meter. Data from nine studies are available for datapoints below 1-meter and data from five studies are available below 2-meters. Of the 39 chemicals, available data for 22 chemicals indicate no measurable hydrolysis under typical environmental conditions (typically determined at pH 5, 7, and 9). For such chemicals, any observed degradation is occurring via processes other than aqueous hydrolysis. Currently, standard GW modeling assumes that only aqueous hydrolysis occurs below 1-meter.

#### 3.2.1 Metabolism Rate with Depth

[ REF\_Ref35873998 \h \\* MERGEFORMAT ] depicts plots of the relative rate of metabolism (subsurface rate expressed as a percentage of surface rate) plotted versus the midpoint of the depth segment from which the subsurface sample was taken. For example, the midpoint of a sample collected between 10 and 20 cm, is 15 cm. Each point reflects one subsurface and surface soil pair from the open literature data. One soil may have multiple data points, as degradation may have been measured at multiple depths and multiple chemicals will have multiple data points in the graph. For example, there are multiple datapoints for atrazine. All y-values greater than 200 were plotted at 200.

In [ REF\_Ref35873998 \h \\* MERGEFORMAT ], y-values below 100 indicate that the subsurface metabolism was slower than surface metabolism (137 datapoints) and y-values above 100 indicate the subsurface metabolism was faster than that measured in the surface soil sample (22 datapoints).

The current PWC model degradation assumption for ASM is illustrated as a dashed black line (labeled as 1m zone of ASM), going from 100% of the ASM surface rate at zero cm depth, to 0% of that rate at 100 cm (1 meter). The current GW conceptual model assumes that aqueous hydrolysis is the only degradation process that occurs below 1-meter. The purple line shows the construct assuming that the zone of ASM degradation is 2-meters. The model assumption is conservative (*i.e.*, predicts slower subsurface metabolism) for datapoints above the line and

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<sup>f</sup> Thirteen of 159 reported half-life values were greater than 200-days.

in the green shaded area and nonconservative (predicts faster subsurface metabolism) for datapoints below the model construct line (see **Appendix B** for a visual explanation).

Looking at the data visually, relative rate at shallow depths is similar to degradation rates at the surface while degradation rates in the deeper depths tend to be slower than the degradation rates at the surface. As the depth increases, the relative rates decrease suggesting a decrease in metabolism with depth, especially for datapoints below 60 cm. However, there is a lot of variability in the data. The data also show that metabolism may continue at greater depths for some pesticides in some environments. Half-life values reported from soils collected between midpoint -depths of 200 to 463-cm ranged from 10 to 990 days (median=72-days) with only one value above 248-days. [ REF \_Ref46996245 \h \\* MERGEFORMAT ] shows a regression through all available datapoints with the intercept forced to 100, to reflect the assumption that the surface degradation rate is equal to the value measured at the surface. The regression supports that overall, most pesticide degradation slows down with depth. Considering the entire regressed line, the 2-meter zone of metabolism is closer to the regressed line than the 1-meter zone of metabolism assumption. While the regression shows the central tendency across available data, few datapoints are available for pesticides below 1 and 2-meters and the relationship for individual pesticides and soils is highly variable. It is uncertain what the central tendency would be if a more robust dataset were available.

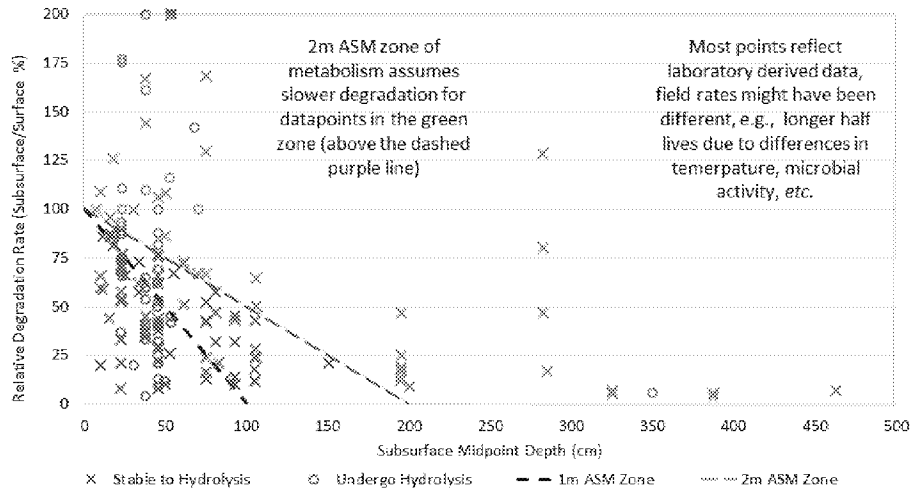


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Summary of Open Literature Data Relative Degradation Rate by Subsurface Depth for Pesticides Stable to Hydrolysis and Pesticides Undergoing Hydrolysis  
y-values greater than 200 were shown at 200

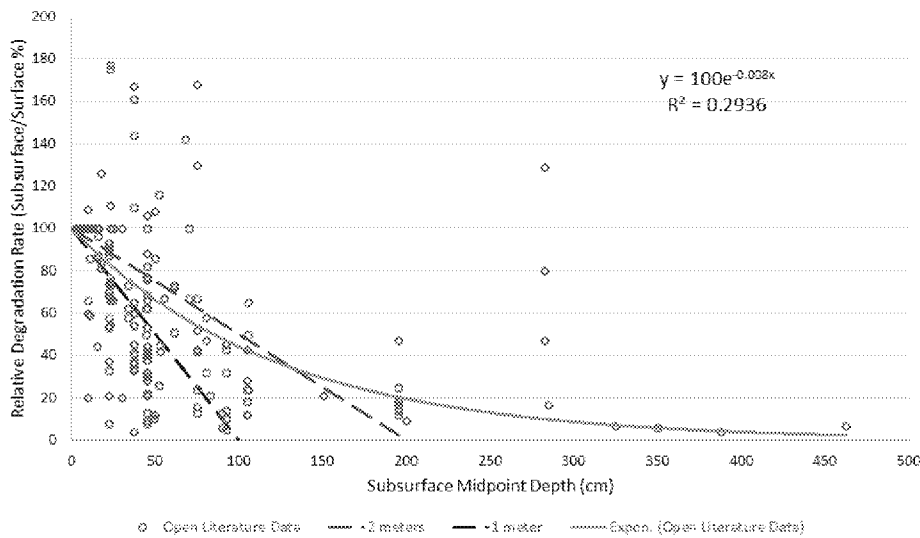


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Summary of Open Literature Data Relative Degradation Rate by Subsurface Depth – Regression Line

[ PAGE \\* MERGEFORMAT ]



[ REF\_Ref35874785 \h \\* MERGEFORMAT ] is the same general figure as shown in [ REF\_Ref35873998 \h \\* MERGEFORMAT ], except data are plotted for each soil by depth, for datasets which had subsurface data measured at depths below 1-meter and the chemical was stable to hydrolysis. Each figure summarizes results for one pesticide. These figures provide an understanding of the change in degradation in a soil with depth, especially for datasets with data below 1-meter. In this analysis, a set of data points with the same color represents one soil for that pesticide. In these graphs, there are 22 datapoints (across all chemicals and soils shown in **Appendix B**) where the subsurface metabolism was faster than the corresponding surface metabolism<sup>8</sup>. A graph for each chemical and soil combination collected from the open literature (regardless of the subsurface depth and including those chemicals that undergo hydrolysis) is provided in **Appendix B**.

Data examining subsurface metabolism below 150-cm is only available for 12 soils and five chemicals (acetochlor, alachlor, atrazine, metribuzin, and metolachlor). [ REF\_Ref35874785 \h \\* MERGEFORMAT ] summarizes these results for chemicals stable to hydrolysis. Data for two soils provide evidence that substantial amounts of metabolism may occur in the subsurface at depths near 200 cm. The subsurface rate was 80% of the surface rate at 283-cm in an acetochlor study and the subsurface rate was 47% of surface rate at 195-cm for an alachlor study. However, data for the other chemicals and soils indicates that subsurface degradation will be substantially slower at these lower depths. For example, the subsurface rate was 17% of the surface rate at 285 cm in one study for atrazine), the subsurface rate was <10% of surface rate at depths from 200-462-cm in one study for metolachlor. Some degradation or transformation was observed at all depths for several pesticides, including pesticides stable to hydrolysis.

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<sup>8</sup> One explanation for why we might see a faster degradation in the subsurface would be if there was a reduced amount of organic carbon and higher bioavailability at lower depths.

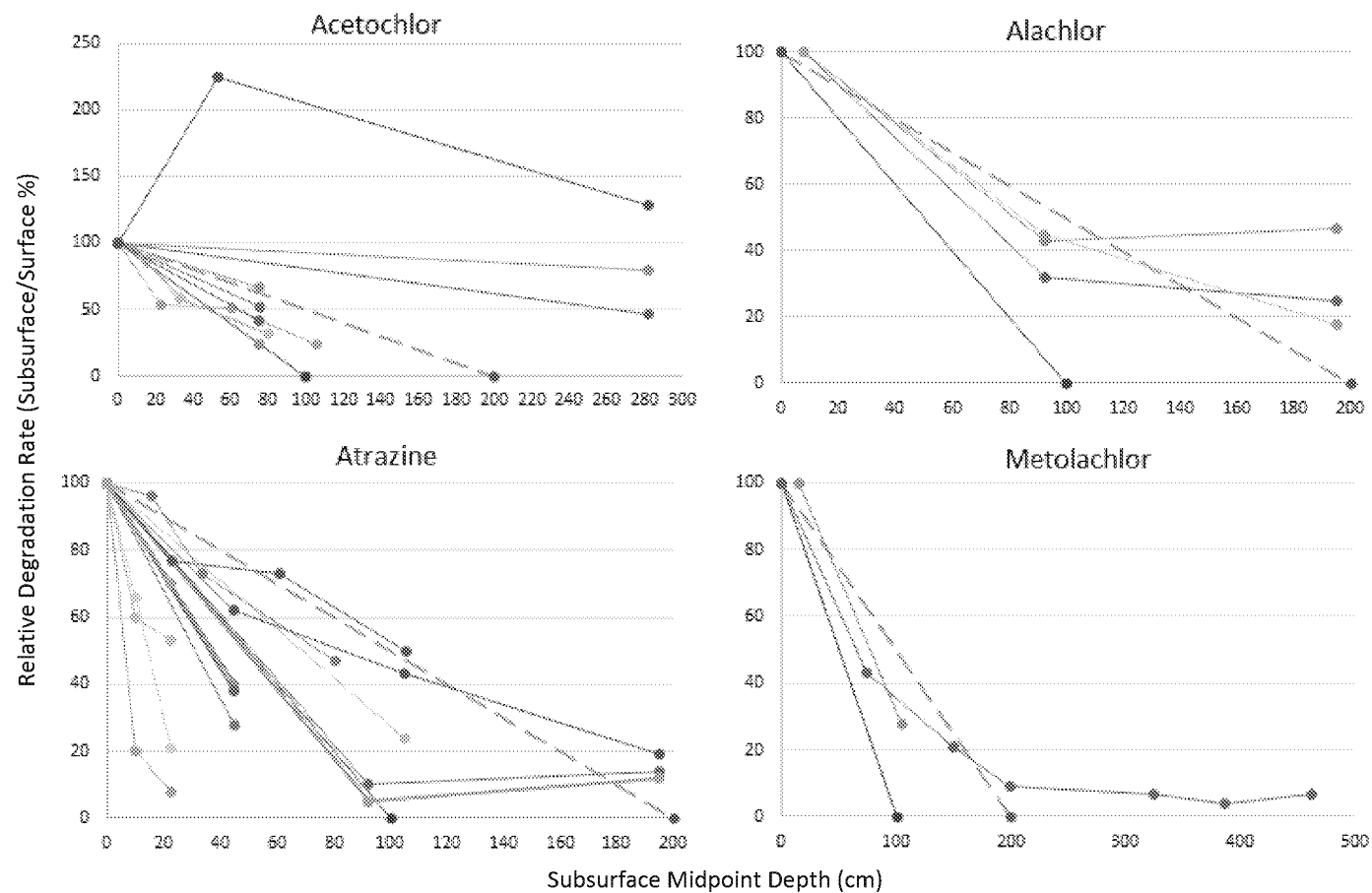


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Open Literature Subsurface Rate Expressed as a Percentage of Surface Rate for Different Soils at Varying Depths

Results included if data available below 1-meter

### 3.2.2 Half-life with Depth

We compared the subsurface half-life to the surface half-life to inform the subsurface modeling assumption that a low level of background metabolism may occur throughout the soil profile. [ REF\_Ref36456110 \h \\* MERGEFORMAT ] depicts the ratio of the subsurface half-life to the corresponding surface half-life which is plotted by the deepest subsurface depth sampled. For the shallower subsurface samples (<50 cm), the half-lives are clearly closer to the surface soil half-lives than for the deeper subsurface samples. Using this graph, a conservative assumption on the factor that the subsurface rate should be in relation to the surface rate could be explored. If the factor applies or does not apply across depths analyzed, that is informative as well.

The subsurface to surface half-life ratio only exceeds 10x for

- 7 of 39 datapoints<sup>h</sup> (18
- % of data with subsurface depths at or below 1-meter<sup>i</sup>); and
- 5 of 17 datapoints (29% of data with subsurface depths at or below 2-meters<sup>j</sup>).

Some degradation is occurring in the subsurface for some pesticides and in some soils as the subsurface half-life of only 10 chemicals show stability in the subsurface ( $\geq 180$  days). These data could be used to support an assumption that the subsurface half-life beyond 1-meter is 10x the surface half-life. While, the amount of data available below 1-meter and especially 2-meters is limited, datapoints below 0.75 meters converge also indicate that a 10x the surface half-life assumption would be protective for most pesticides. Additionally, the assumption was not protective for 18% of data available below 1-meter or 29% of datapoints below 2-meters. In [ REF\_Ref36456110 \h \\* MERGEFORMAT ], for some soils and for some pesticides metabolism is occurring at all depths in addition to hydrolysis (assuming a 30-day hydrolysis study is sufficient to show stability to hydrolysis)<sup>k</sup>. One half-life measured below 2-meters was greater than 500-days, all other half-life values measured below 2-meters were below 223-days. For these data points, the majority of the subsurface to surface half-life ratios are greater than 1 (86%); indicating that degradation is occurring more rapidly in the surface and the chemicals are degrading more slowly at deeper depths; as also indicated in [ REF\_Ref36456110 \h \\* MERGEFORMAT ]. The chemicals stable to hydrolysis (based on a 30-day hydrolysis study) are also those chemicals with the most degradation activity at depths greater than 100 cm.

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<sup>h</sup> Nine studies collected soils from with midpoint depth below 1-meter and 12 studies had the lowest sampling depth collected below 1-meter.

<sup>i</sup> The subsurface depth for these analyses considered the lowest depth sampled for the subsurface samples.

<sup>j</sup> Five studies collected soils from the midpoint depth or lowest sampling depth below 2-meters.

<sup>k</sup> The 30-day hydrolysis studies may not reliably predict whether hydrolysis may occur over the 30 to 100-year simulation assumed in PWC modeling.

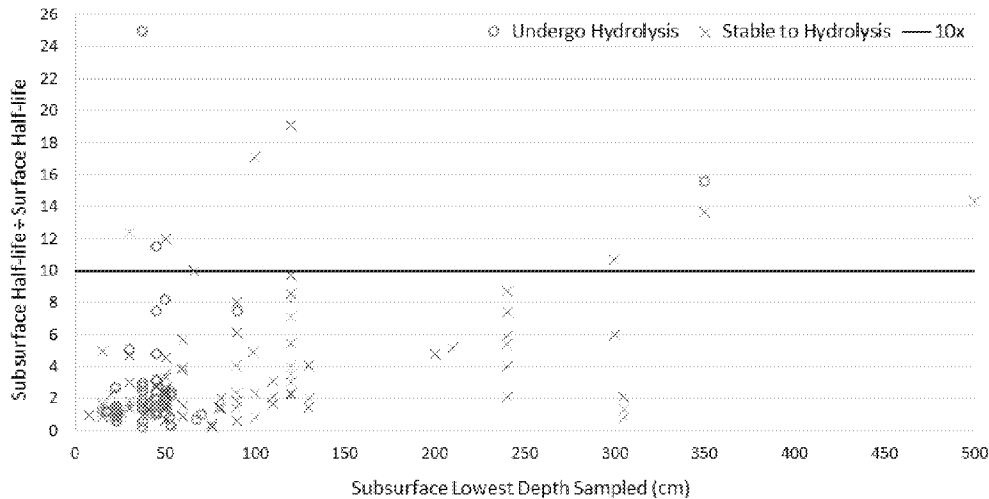


Figure [ STYLERE 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Ratio of Subsurface Half-Life to Surface Half-life by Subsurface Lowest Depth Sampled

### 3.2.3 Metabolism Rate and Soil Characteristics

Next, it was assessed whether soil characteristics other than surface and subsurface rates might be related to metabolism rate. Organic carbon tends to be lower in the subsurface versus surface soils. This could change degradation rates. Decreased amounts of organic carbon in the subsurface could result in increased bioavailability of pesticides due to diminished sorption and thus degradation at lower depths[ ADDIN EN.CITE

<EndNote><Cite><Author>Council</Author><Year>2003</Year><RecNum>5312</RecNum><DisplayText><style face="superscript">50</style></DisplayText><record><rec-number>5312</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184602" guid="060ac29e-a563-47e1-ab72-b86864864716">5312</key></foreign-keys><ref-type name="Edited Book">28</ref-type><contributors><authors><author>National Research Council</author></authors></contributors><titles><title>Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications</title></titles><dates><year>2003</year></dates><pub-location>Washington, D.C.</pub-location><publisher>The National Academies Press</publisher><urls><related-urls><url>https://www.nap.edu/catalog/10523/bioavailability-of-contaminants-in-soils-and-sediments-processes-tools-and</url></related-urls></urls></record></Cite></EndNote>].

Alternatively, higher carbon content at the surface or higher temperatures (in the field) at the surface could result in higher microbial activity as compared to the subsurface[ ADDIN EN.CITE <EndNote><Cite><Author>Blume</Author><Year>2002</Year><RecNum>5313</RecNum><Dis

playText><style face="superscript">51</style></DisplayText><record><rec-number>5313</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184602" guid="c87ae91d-c7b4-4e65-8055-cc20eaf7fd99">5313</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Blume, E.</author><author>Bischoff, M.</author><author>Reichert, J. M.</author><author>Moorman, T.</author><author>Konopka, A.</author><author>Turco, R. F.</author></authors></contributors><titles><title>Surface and subsurface microbial biomass, community structure and metabolic activity as a function of soil depth and season</title><secondary-title>Applied Soil Ecology</secondary-title></titles><periodical><full-title>Applied Soil Ecology</full-title></periodical><pages>171-181</pages><volume>20</volume><number>3</number><keywords><keyword>Subsurface soils</keyword><keyword>Soil microbial activity</keyword><keyword>Seasonal response</keyword><keyword>Soil microbiology</keyword></keywords><dates><year>2002</year><pub-dates><date>2002/06/01</date></pub-dates></dates><isbn>0929-1393</isbn><urls><related-urls><url>http://www.sciencedirect.com/science/article/pii/S0929139302000252</url></related-urls></urls><electronic-resource-num>https://doi.org/10.1016/S0929-1393(02)00025-2</electronic-resource-num></record></Cite></EndNote>]. An analysis on the amount of organic carbon and depth did not show any trends in the data. This does not indicate that organic carbon is not an important consideration, only that, it is not possible to understand the impact of these factors without considering and controlling other factors. For example, the percent organic carbon may be important for some soils and chemicals and less important for others.

### 3.3 Conclusions

Open literature data were analyzed to better understand how subsurface ASM rates relate to surface ASM rates. The following conclusions were drawn from the data.

- In general, subsurface metabolism is slower than surface metabolism and still occurs at measurable rates throughout the depths tested. There is a general decline in the rate with depth, with great variability between chemicals and soils.
- Limited data (22 datapoints considering the midpoint depth and 39 datapoints considering the lowest depth of the surface sample) are available below 1-meter and even fewer datapoints below 2-meters (17-datapoints). Generally, degradation below 1-meter is slower than the surface; however, metabolism or degradation was observed at all depths evaluated for some pesticides and soils.

These conclusions support the exploration of alternative modeling assumptions for the subsurface. Degradation other than hydrolysis<sup>1</sup> was observed for some pesticides and for some soils below 1-meter supporting exploration of alternative depths on when the ASM declines to

<sup>1</sup> Assuming the 30-day hydrolysis study is adequate to show stability to hydrolysis.

zero. The majority of subsurface metabolism half-life values are within a factor of 10 of the surface ASM, supporting exploration of the alternative input parameter for setting a background degradation rate in the subsurface.

## 4 Modified Modeling Versus Current Standard Modeling

**Section 4** summarizes how changing the standard subsurface modeling assumptions in PWC modeling impacts EDWCs. The following model assumption abbreviations are used throughout this document:

- 1m0x – current modeling assumptions of ASM declining to zero at 1 m depth and no change to the abiotic hydrolysis input
- 2m0x, 3m0x, and 4m0x – ASM declining to zero at 2, 3, and 4 meters, respectively, from the surface and no change to the abiotic hydrolysis input
- 1m10x – ASM declining to zero at 1 m from the surface and the hydrolysis half-life was assumed to be 10x the ASM half-life. Examined only for chemicals that do not undergo hydrolysis. The hydrolysis half-life was faster than 10x the ASM for all of the pesticides that underwent hydrolysis.
- 2m10x, 3m10x, and 4m10x – defined similarly as above.

**Section 4.1** describes how ASM and hydrolysis half-life values influence EDWCs and interact with sorption. **Section 4.2** summarizes the impact of changing modeling assumptions on EDWCs. A more detailed analysis of these results is available in **Appendix D**

### 4.1 Influence of Aerobic Soil Metabolism, Hydrolysis Half-life, and Sorption on EDWCs

For any given scenario, all chemicals move at similar velocities with the downward movement of water in the dissolved phase. Therefore, all chemicals will spend similar amounts of time subject to dissolved phase degradation. Since hydrolysis only occurs in the dissolved phase, Koc largely does not impact EDWCs affected solely by abiotic hydrolysis alone. However, Koc controls the amount of time that a chemical spends in the sorbed phase with higher Koc values leading to more time for sorbed phase ASM degradation. Because ASM is modeled as occurring in both the dissolved and sorbed phases, ASM is greatly enhanced (reduced EDWCs) at higher Koc values. For low Koc values, an abiotic hydrolysis half-life alone (no ASM) will produce a greater reduction in EDWC than the numerically similar ASM half-life alone (no hydrolysis) due to hydrolysis occurring throughout the entire soil profile and not declining with depth as ASM degradation is modeled. Conversely, at high Koc values (somewhere >1000 L/kg-oc), an ASM half-life produces a greater reduction in EDWC than a numerically similar abiotic hydrolysis half-life (related to the long residence time of the chemical in the upper soil layers where the ASM rate is greatest).

### 4.2 Impact of Changes in Subsurface Modeling Assumptions on EDWCs

[ PAGE \\* MERGEFORMAT ]

The impact of changing the zone of ASM on EDWCs depends on the ASM and  $K_{oc}$  of the pesticide. Pesticides that undergo abiotic hydrolysis and are stable to ASM are insensitive to changes in ASM depth. For pesticides with a long ASM half-life (1000 and 5000-days), EDWCs were within 10% of the 1m0x EDWCs up to a  $K_{oc}$  of 1000 L/kg-organic carbon. For ASM half-life values below 1000-days, EDWCs begin to be influenced by the zone of ASM and how they are influenced changes depending on the ASM half-life and  $K_{oc}$  combination. The amount of decrease in EDWCs increases as the ASM decreases and as  $K_{oc}$  increases. [ REF\_Ref45477633 \h \\* MERGEFORMAT ] summarizes the fraction of the standard 1 m ASM depth EDWC remaining after the ASM depth is incrementally increased to 2, 3, and 4 meters and can be used to understand how an assumption would influence EDWCs with different combinations of properties.

Table [ STYLeref 1 \s ]-[ SEQ Table \\* ARABIC \s 1 ]. Variation in the Fraction of 1-meter ASM Depth Peak and PBA EDWC Remaining with Different Modeling Assumptions and Combinations of  $K_{oc}$  and ASM half-life

Modeling Assumption	ASM $T_{1/2}$ (days)	Fraction of 1m0x Peak EDWC Remaining (Post-Breakthrough Average)							
		$K_{oc}=0$		$K_{oc}=100$		$K_{oc}=500$		$K_{oc}=1000$	
2m0x	10	0.36	(0.16)	0.10	(0.07)	0.01	(<0.01)	<0.01	(<0.01)
	50	0.59	(0.58)	0.48	(0.45)	0.19	(0.18)	0.07	(0.07)
	100	0.72	(0.74)	0.62	(0.64)	0.39	(0.38)	0.21	(0.21)
	200	0.83	(0.86)	0.77	(0.79)	0.59	(0.59)	0.42	(0.42)
	500	<b>0.92</b>	<b>(0.94)</b>	<b>0.90</b>	<b>(0.91)</b>	0.79	(0.80)	0.67	(0.68)
	1000	<b>0.96</b>	<b>(0.97)</b>	<b>0.95</b>	<b>(0.95)</b>	0.88	(0.89)	0.81	(0.82)
	5000	<b>0.99</b>	<b>(0.99)</b>	<b>0.99</b>	<b>(0.99)</b>	<b>0.98</b>	<b>(0.98)</b>	<b>0.96</b>	<b>(0.96)</b>
3m0x	10	0.25	(0.03)	0.05	(0.01)	<0.01	(<0.01)	<0.01	(<0.01)
	50	0.39	(0.28)	0.25	(0.17)	0.04	(0.03)	0.01	(<0.01)
	100	0.55	(0.50)	0.44	(0.38)	0.17	(0.14)	0.05	(0.04)
	200	0.72	(0.70)	0.62	(0.60)	0.38	(0.35)	0.19	(0.18)
	500	0.86	(0.86)	0.82	(0.81)	0.65	(0.64)	0.48	(0.48)
	1000	<b>0.93</b>	<b>(0.93)</b>	<b>0.90</b>	<b>(0.90)</b>	0.80	(0.80)	0.68	(0.68)
	5000	<b>0.98</b>	<b>(0.99)</b>	<b>0.98</b>	<b>(0.98)</b>	<b>0.96</b>	<b>(0.95)</b>	<b>0.92</b>	<b>(0.93)</b>
4m0x	10	0.20	(0.01)	0.04	(<0.00)	<0.01	(<0.01)	<0.01	(<0.01)
	50	0.30	(0.21)	0.14	(0.10)	0.01	(0.01)	<0.01	(<0.01)
	100	0.44	(0.44)	0.31	(0.29)	0.08	(0.07)	0.01	(0.01)
	200	0.63	(0.65)	0.50	(0.53)	0.25	(0.24)	0.09	(0.09)
	500	0.81	(0.84)	0.75	(0.77)	0.54	(0.55)	0.35	(0.36)
	1000	<b>0.90</b>	<b>(0.92)</b>	0.86	(0.87)	0.73	(0.73)	0.58	(0.59)
	5000	<b>0.98</b>	<b>(0.98)</b>	<b>0.97</b>	<b>(0.97)</b>	<b>0.94</b>	<b>(0.94)</b>	<b>0.89</b>	<b>(0.90)</b>
1m10x	10	0.45	(0.15)	0.27	(0.13)	0.17	(0.12)	0.17	(0.11)
	50	0.69	(0.61)	0.67	(0.62)	0.64	(0.61)	0.65	(0.60)
	100	0.76	(0.78)	0.81	(0.78)	0.80	(0.77)	0.80	(0.78)
	200	0.86	(0.88)	0.91	(0.88)	0.88	(0.88)	0.89	(0.88)
	500	<b>0.94</b>	<b>(0.95)</b>	<b>0.96</b>	<b>(0.95)</b>	<b>0.95</b>	<b>(0.95)</b>	<b>0.95</b>	<b>(0.95)</b>
	1000	<b>0.97</b>	<b>(0.97)</b>	<b>0.98</b>	<b>(0.97)</b>	<b>0.97</b>	<b>(0.97)</b>	<b>0.97</b>	<b>(0.98)</b>
	5000	<b>0.99</b>	<b>(0.99)</b>	<b>1.00</b>	<b>(0.99)</b>	<b>1.00</b>	<b>(0.99)</b>	<b>0.99</b>	<b>(1.00)</b>

Values within 10% of the standard modeling assumption (1m0x) are shown in bold.

Assuming a background metabolism rate resulted in smaller reductions in EDWCs as compared to changing the depth which ASM is assumed to occur ([ REF \_Ref45477633 \h \\* MERGEFORMAT ]). As the background degradation rate only applies to the dissolved phase, Koc does not impact EDWC to the extent that it does when changing ASM depth.

Peak and PBA EDWCs with the 1m10x were 80 to 90% of the 1m0x EDWCs for ASM half-life values greater than 200-days and 60 to 70% for ASM half-life values of 50 and 100-days across Koc values. The fraction of the 1m0x EDWCs for ASM half-life near 10-days decreases from 0.45 to 0.17 as the Koc value increases; however, these EDWCs also tend to be very low, even when the hydrolysis is assumed to be stable. The PBA EDWCs for the 10-day ASM range from 0.11 to 0.15 the 1m0x EDWCs.

## 5 Prospective Groundwater Monitoring Versus Modeling Results

Prospective Ground Water (PGW) studies (OCSPP 835.7100) are field studies in which a pesticide and a GW flow tracer (usually bromide) are applied to a field instrumented with piezometers and nested wells, at increasing depths, to determine the ability of the pesticide to leach through the soil and contaminate GW.

PGW studies are usually conducted in areas that are known to be vulnerable to leaching of contaminants through soil, such as the sand and sandy loam soils in the six PWC GW scenarios. Over time, many PGW studies have been conducted in geographic areas that are represented by the PWC scenarios, such as the Florida Central Ridge or Wisconsin sands areas.

EFED has found it useful to compare the results of PGW studies with PWC model runs, when the PWC scenarios represent the same area as the location of the PGW study, to “ground-truth” the results of the model run. This is usually done by parameterizing the model to replicate the conditions of the PGW study as closely as possible, in terms of number and rate of applications, application date, year of application, etc. Often, there is good agreement between results of the PGW study and PWC run, based on a single year of application[ ADDIN EN.CITE ADDIN EN.CITE.DATA ]. In this chapter, PWC results with standard and modified modeling assumptions were compared to PGW monitoring results.

### 5.1 Methods

This ground-truthing technique was used in the current work to determine whether model input parameter changes, or model’s construct changes, provide results that are similar to or conservative of those observed in the PGW studies. This included (1) the assumption of a hydrolysis half-life ten times greater than the ASM half-life for chemicals stable to hydrolysis, (2) increasing the depth of the metabolism zone to 2, 3, or 4 meters, and (3) a combination of (1) and (2). In these simulations, the application rate and the PWC scenario were selected to match the PGW study.

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PGW studies for 10 chemicals, representing four of the six PWC scenarios were examined. Model runs were set up to replicate the conditions of the PGW study as far as possible, without modification of the underlying model parameterization aside from metabolism depth. Modeling was conducted assuming yearly applications for 30-years and alternatively applications spaced out so that the pulses of the contaminants in the subsurface did not overlap and influence each other. Here, the "breakthrough time" from the PWC run was used to set up model runs with applications spaced in time to reflect results from a single year of applications, reflecting what occurred in the PGW studies. For example, if the breakthrough time was seven years, the applications were set to one every seven years to avoid overlap of the concentration traces and therefore the magnitude of the peak. If a single year of applications were simulated to match the PGW, there would not be an understanding of the impact of the variation in the weather

The simulation with 30-years of applications is used to show whether standard modeling is likely to estimate concentrations higher than those observed in the PGW studies. These simulations are expected to predict concentrations higher than those measured in the PGW studies, as 30 applications are simulated but only one application was usually made in the PGW study. For the simulation set up with applications spaced with the breakthrough time, the PWC estimated concentrations are expected to produce results that are similar to the concentrations observed in the PGW studies.

PWC was modified to allow increase of the metabolism zone depth. A zone of degradation (cm) parameter was added to the Advanced tab. This setting increased the depth at which the ASM rate of metabolism decreased to zero from one meter (100 cm) to the selected depth.

PGW studies are conducted for chemicals that may have the potential to leach to GW, based on the results of terrestrial field dissipation (TFD) studies or environmental fate properties (mobility and persistence). Thus, the chemicals represented in the PGW studies examined tend to be mobile and persistent, or to have mobile, persistent transformation products. This analysis is therefore largely limited to this subset of chemicals. The chemicals analyzed have ASM model input half-life values ranging from 47 days to 552 days and all but two chemicals are stable to hydrolysis.

Analysis was completed by comparing peak PWC GW concentrations and maximum PGW concentrations. Reliable post-breakthrough average concentrations were not readily available in most PGW studies and the studies only followed residues for a few years while the PWC simulates 30 or 100-years. Taking a percentage of the detections in a soil profile at a site could be misleading as the percentile is dependent on the number of samples collected, when sampling occurred in relation to precipitation, and the number of detections in a soil profile. Additionally, taking a percentile from monitoring results reflecting a few years of data and a few samples collected per year is not directly comparable to a percentile of concentrations with daily concentration estimates over an extended period. While there is still some discrepancy in comparing the peak measured concentration with the peak PWC estimated concentration, at least the comparison is the peak value from each data set. There is uncertainty in whether a

[ PAGE \\* MERGEFORMAT ]

higher concentration may have occurred in the PGW if daily samples may have been collected at the PGW site; however, the studies are 1) designed to be able to follow the pesticide residues that occur over time at a site; 2) to capture the range of concentrations that may occur at a site; and 3) are some of the most robust datasets available for evaluating the ability of the PWC to predict pesticide concentrations in groundwater. We acknowledge that there are uncertainties in the comparisons with maxima; the potential benefits from the use of percentiles versus maxima was judged to be outweighed by the limitations of the empirical data sets.

For the results where the PGW maximum measured concentration exceeded the peak modeled concentration, the PGW results and modeling were revisited to see if there was an explanation as to why the results were different.

## 5.2 Results

[ REF\_Ref36210915 \h \\* MERGEFORMAT ] and [ REF\_Ref36210810 \h ] present the results of PWC modeled peak concentrations compared to the maximum concentrations observed in the in PGW studies (yellow bar). All inputs and results are provided in [ REF\_Ref37175331 \h \\* MERGEFORMAT ]. Pesticide concentrations are provided on the y-axis in log scale. A value of one was added to all graphed results to make all results positive, as log values below one are negative. Bars are grouped by pesticide-PGW combination on the x-axis in order of increasing pesticide persistence. For most chemicals, the modeled concentrations were higher than the observed concentrations. The blue bars show the peak PWC modeling EDWCs simulated with the zone of metabolism set to the standard one meter, along with increased depths of 2, 3, and 4 meters (shown with the blue bars moving from the 1m standard assumption in dark blue to the 4m zone of ASM in light blue). The green bars show results assuming a background degradation rate of 10x the ASM half-life combined with increasing the zone of metabolism from 1-meter to 4-meters with progressively lighter green with increasing depth. Fenamiphos and sulfentrazone do not have the green bars because they were not stable to hydrolysis.

[ REF\_Ref36276454 \h \\* MERGEFORMAT ] summarizes the fate properties and scenarios used for the simulations, as well as, measured concentrations from the PGW studies and modeling results. The pesticides evaluated are all mobile and on the low end of moderately mobile ( $K_{oc} \leq 132$  L/kg-oc), except for imidacloprid with a  $K_{oc}$  of 266 L/kg-oc and norflurazon which has a  $K_{oc}$  value of 776 L/kg-oc. When looking at the differences in the modeling results with increasing zone of metabolism, generally, the impact is greatest for chemicals that degrade quickly and declines as you move across the x-axis with increasing ASM half-life (see [ REF\_Ref36210915 \h \\* MERGEFORMAT ] and [ REF\_Ref36210810 \h ]). However, the results for norflurazon and imidacloprid do not follow this trend, likely because of the lower mobility of these two pesticides and therefore, increased sorbed phase degradation assumed in the model.

As can be seen in [ REF\_Ref36210915 \h \\* MERGEFORMAT ], the results obtained with the standard one-meter zone (darkest blue bar) are consistently more conservative than (higher than) the PGW maximum concentration (orange bar) when assuming 30-years of applications.

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Increases in the depth of the metabolism zone (progressively lighter blue bars) result in progressive decreases in the modeled peak concentration. Note that the scale is logarithmic, and that the decrease is ten- to one hundred-fold in some cases (e.g., fenamiphos). Generally, the result for the “10x ASM” model run at one-meter (darkest green bar) is equivalent to assuming a standard two-meter metabolism depth. Norflurazon, with the lower mobility, does not follow this trend as the 2m0x EDWC (19 µg/L) is much lower than 1m10x EDWC (128 µg/L), likely due to the longer duration that it is in the metabolism zone for the 2m0x assumption. The 1m10x assumption only influences degradation in the dissolved phase. The “10x ASM” runs with increasing the zone of metabolism are seen to have the same trend as increasing the zone of metabolism without a hydrolysis input assumption, but with a lower EDWC.

The 30-year simulations do not match the application scenarios in PGW studies, which generally have one year of applications, and follow the concentrations in GW for a few years. These PWC simulations are expected to estimate higher concentrations than observed in the PGW studies for persistent pesticides where applications each year may result in increases in residues in GW over time. For the 30-year simulations, most PWC peak EDWCs were higher than the PGW maximum measured concentrations. The fenamiphos peak PWC EDWCs were lower than the PGW maximum for the 3m0x and 4m0x assumption. Fenamiphos has an ASM half-life of 47-days ([ REF\_Ref36210915 \h \\* MERGEFORMAT ]). Fenamiphos is not stable to hydrolysis and thus the analysis of the impact of hydrolysis assumptions was not possible. Additionally, the sulfentrazone PWC EDWCs of 36 µg/L was 3% lower than the maximum PGW concentration of 37 µg/L.

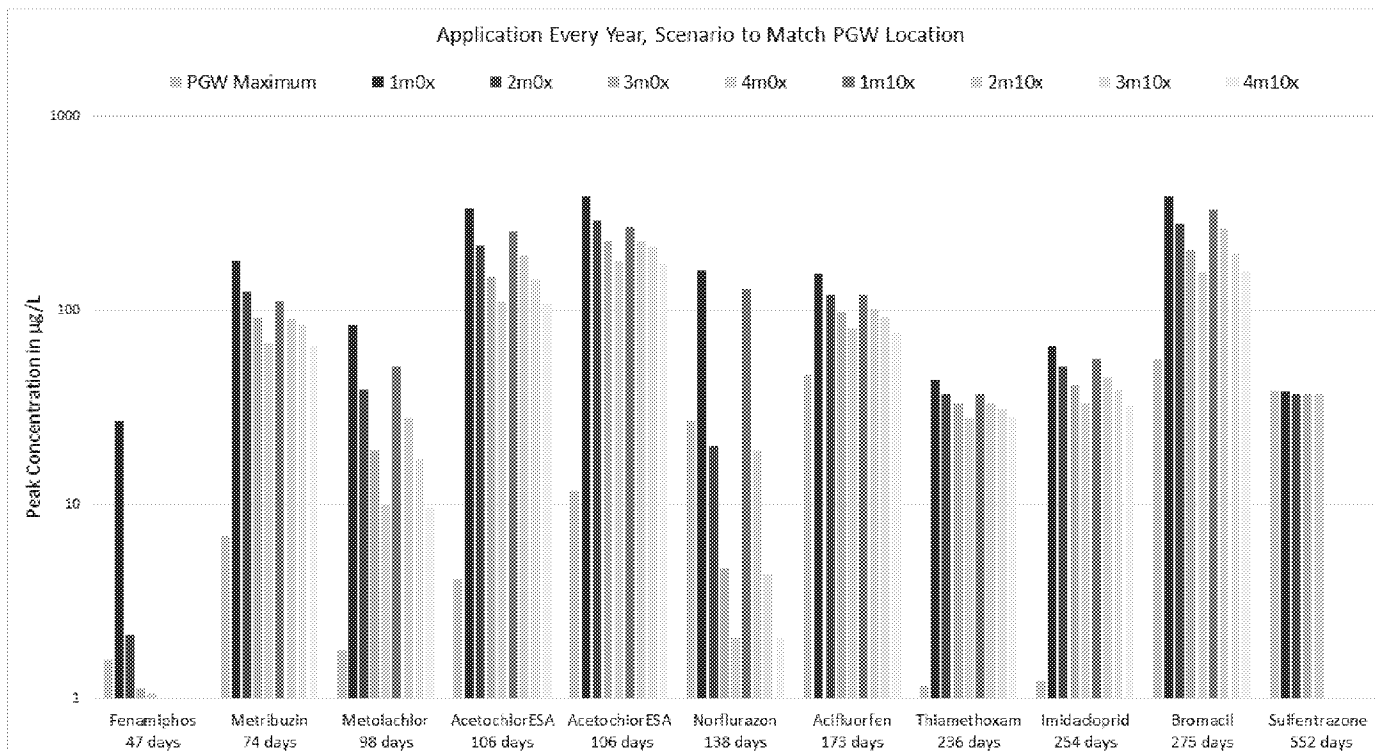


Figure [ STYLEREFF 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Comparison of Maximum PGW Concentration and PWC Peak Concentration Assuming 30-years of Applications

The x-axis shows the pesticide name followed by the ASM input half-life from shortest to longest duration.

Table [ STYLEREf 1 \s ]-[ SEQ Table \\* ARABIC \s 1 ]. Maximum PGW Concentrations and Peak Concentration from PWC Modeling Using Different Modeling Assumptions

Pesticide	PWC Scenario	Mean K <sub>oc</sub> (L/k)	Half-Life (days)		Pesticide Concentration in Groundwater (µg/L)								
			ASM Half-Life Input (days) <sup>1</sup>	Hydrolysis Half-life (days)	Max PGW	1m0x	2m0x	3m0x	4m0x	1m10x	2m10x	3m10x	4m10x
Peak Concentrations – Applied Every Year for 30-years													
Fenamiphos	FL Central Ridge	Kd = 0.958	47	300	0.58	26	1.13	0.13	0.06	--	--	--	--
Metribuzin	WI sands	20	74	Stable (0)	5.9	180	125	91	67	111	90	83	65
Metolachlor	GA	132.4	98	Stable (0)	0.78	83	38	18	9.04	50	27	16	8.72
AcetochlorESA	Delmarva	28.8	106	Stable (0)	3.1	336	215	148	111	255	192	144	107
	WI sands				10.7	387	291	227	180	269	226	211	173
Norflurazon	FL Central Ridge	776	138	Stable (0)	26	159	19	3.67	1.05	128	18	3.4	1.05
Acifluorfen	WI sands	109	173	Stable (0)	46	154	120	97	80	120	101	92	77
Thiamethoxam	WI sands	70.23	236	Stable (0)	0.16	43	36	32	27	36	32	30	27
Imidacloprid	WI sands	266	254	Stable (0)	0.24	65	50	40	32	55	44	38	31
Bromacil	FL Central Ridge	41.1	275	Stable (0)	55	384	277	203	158	331	266	196	158
Sulfentrazone	NC Coastal Plain	29	552	375	37.4	37	36	36	36	--	--	--	--
Peak Concentrations – Applications Spaced at Breakthrough Time													
Fenamiphos	FL Central Ridge	Kd = 0.958	47	300	0.58	2.91	0.14	0.02	0.007	--	--	--	--
Metribuzin	WI sands	20	74	Stable (0)	5.9	42	29	20	14	21	18	17	13
Metolachlor	GA	132.4	98	Stable (0)	0.78	14	6.53	3.24	1.68	9.08	4.74	2.96	1.61
AcetochlorESA	Delmarva	28.8	106	Stable (0)	3.1	92	71	58	47	78	66	56	46
	WI sands				10.7	87	66	48	36	56	45	43	34
Norflurazon	FL Central Ridge	776	138	Stable (0)	26	19	2.6	0.57	0.19	15	2.37	0.53	0.19
Acifluorfen	WI sands	109	173	Stable (0)	46	24	18	15	12	18	16	14	12
Thiamethoxam	WI sands	70.23	236	Stable (0)	0.16	8.34	7	5.89	4.95	6.69	6.01	5.64	4.88
Imidacloprid	WI sands	266	254	Stable (0)	0.24	8.13	6.38	5.14	4.17	6.86	5.66	4.93	4.09
Bromacil	FL Central Ridge	41.1	275	Stable (0)	55	111	90	76	64	101	87	73	64
Sulfentrazone	NC Coastal Plain	29	552	375	37.4	10	10	10	9.97	--	--	--	--

PGW=Prospective groundwater study; ASM=aerobic soil metabolism; PWC = Pesticide in water calculator; AcetachlorESA: Acetochlor ethanesulfonic acid

-- Pesticide was not stable to hydrolysis and the modeling simulation was not possible. PWC EDWCs lower than the PGW maximum concentration are in **bold**.

<sup>1</sup> Pesticides are in order of shortest soil half-life to longest soil half-life.

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[ REF \_Ref12968986 \h \\* MERGEFORMAT ] presents a similar analysis as in [ REF \_Ref36210915 \h \\* MERGEFORMAT ], except that the applications are not yearly, but set to the breakthrough time as described above. The same general trends are seen, with the exception that the standard model run (1m, dark blue bar) is not conservative versus the PGW Maximum (orange bar) for a few cases: norflurazon, acifluorfen, and sulfentrazone. The differences are less than a factor of ten in those cases. Changing modeling assumptions results in underprediction of fenamiphos in addition to those underpredicted using the 1m0x assumption. Ratios of the 1m10x EDWCs divided by the PGW maximum concentrations ranged from 0.4 to 41. Ratios of the 2m0x EDWCs divided by the PGW maximum concentrations ranged from 0.24 to 26, with the lowest ratios occurring for chemicals that were susceptible to hydrolysis and thus not included in the background metabolism in the dissolved phase analysis.

To explore why norflurazon, acifluorfen, sulfentrazone and fenamiphos PWC modeled concentrations were lower than the observed PGW measured concentrations, modeling and the PGW parameters were further explored. For norflurazon, the variability in measured K<sub>oc</sub> values ranged from 192 to 1,532 L/kg-oc and the modeled average K<sub>oc</sub> was 776 L/kg-oc. It is likely that the soil in the PGW study had a higher mobility than the average K<sub>oc</sub> simulated [ ADDIN EN.CITE

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type><contributors><authors><author>USEPA</author></authors><secondary-authors><author>DP Barcode 441241,</author></secondary-authors></contributors><titles><title>Registration Review: Tier 2 Drinking Water Assessment for Norflurazon</title><secondary-title>September 27, 2017</secondary-title><tertiary-title>Environmental Fate and Effects Division. Office of Pesticide Programs. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2017</year></dates><urls></urls></record></Cite></EndNote>].

When a K<sub>oc</sub> of 200 L/kg-oc is assumed for modeling the 1m0x, 2m0x, 1m10x, and 2m10x are 164, 79, 132, and 74 µg/L and are all higher than the PGW maximum concentration of 26 µg/L. This case illustrates the need to consider the variability in sorption coefficients when estimating potential concentrations in groundwater. For norflurazon, the average K<sub>oc</sub> may not be reflective of the range of soils where the chemical could be used, and where the PGW study was conducted (where soils had a low organic carbon content). For acifluorfen, modification of the modeling and scenario to match the PGW study did not alter the EDWCs substantially; however, in the study report there were groundwater detections without corresponding detections throughout the soil profile, it is speculated that the movement of the pesticide may have occurred via preferential flow, which is not simulated in the PWC (MRID 41172801)[

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The modeling results were higher than the maximum PGW concentration measured 63% to 77% of the time. While it is important not to underpredict exposure, it is also important not to overpredict exposure. Overpredictions of more than 10x occurred for four pesticides for the 1m0x and 1m10x assumptions, and three pesticides with the 2m0x, 3m0x, 4m0x, 2m10x, 3m10x, and 4m10x assumptions. [ REF\_36280882 \h \\* MERGEFORMAT ] shows the PGW maximum concentration on the x-axis by the corresponding PWC peak GW concentration on the y-axis, simulated with the different modeling assumptions. Including the increased zone of metabolism and the background degradation resulted in a greater number of datapoints within the 10x above or below the 1 to 1 line.

[ PAGE \\* MERGEFORMAT ]



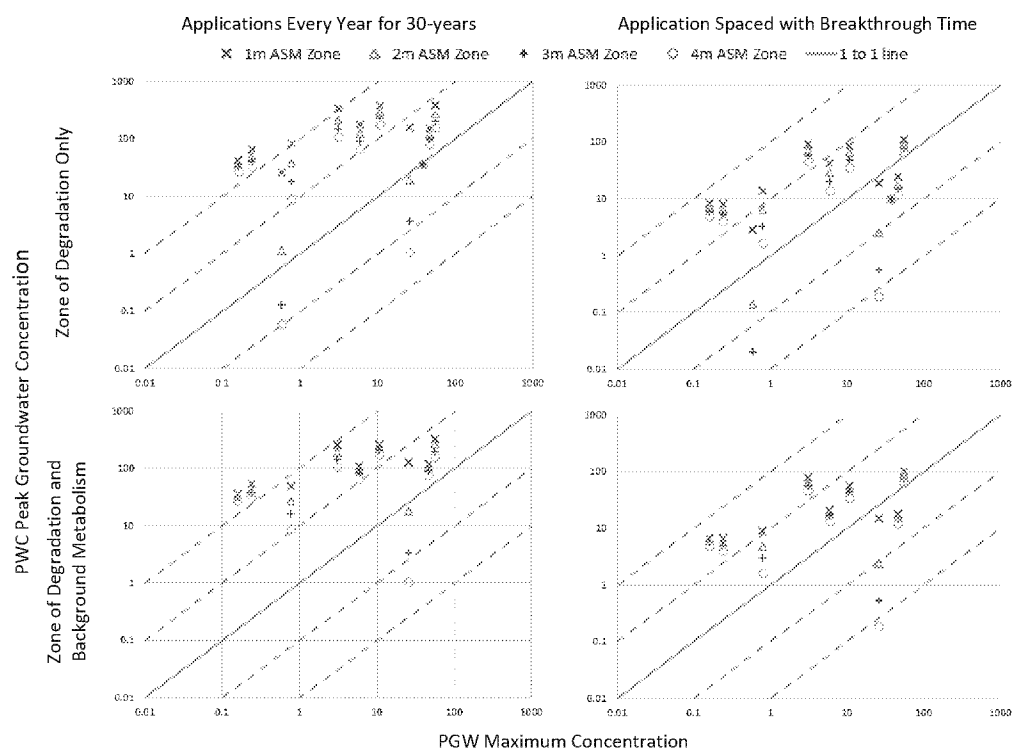


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Comparison of the PGW Maximum Concentration and the PWC Peak Modeled Concentration Considering Different Modeling Assumptions

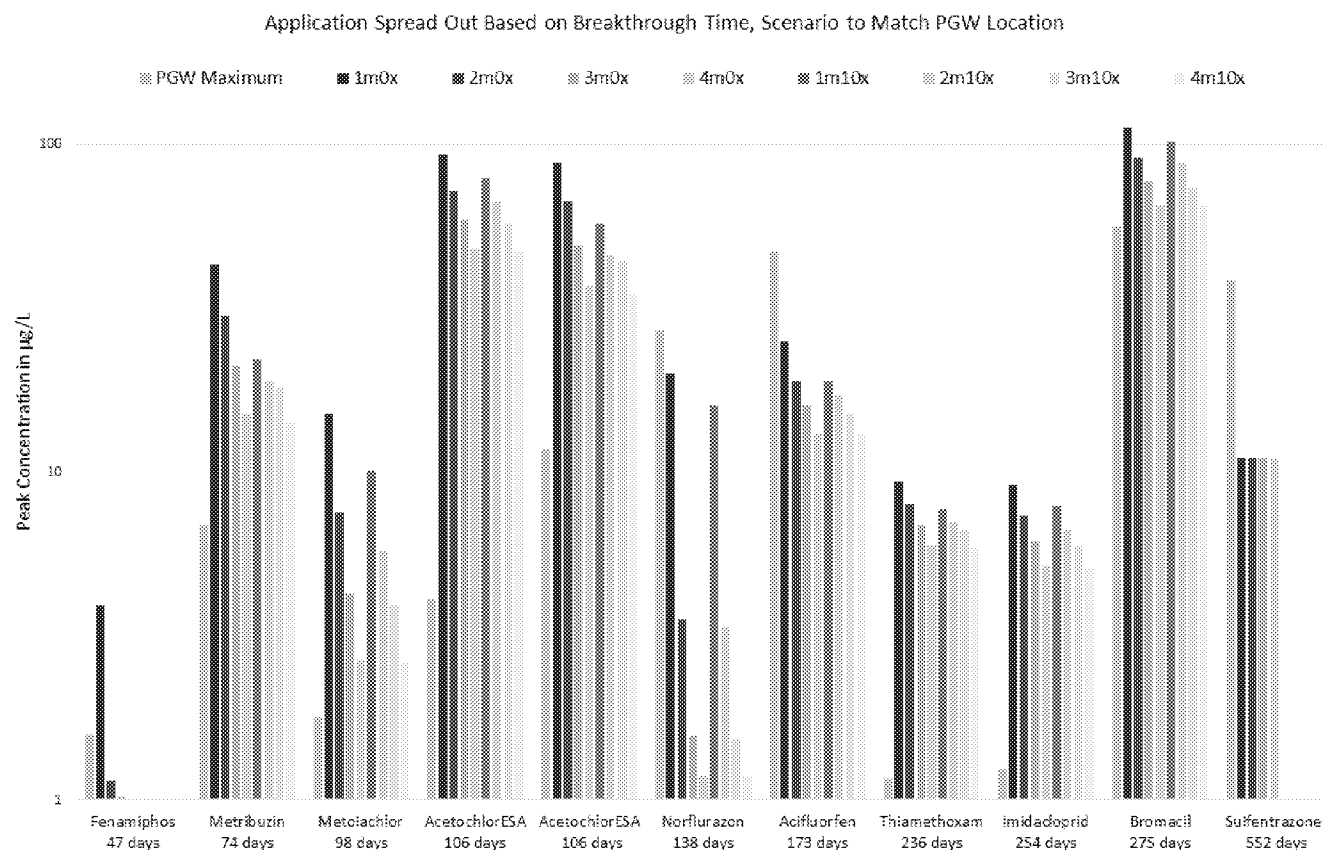


Figure [ STYLEREf 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Comparison of Maximum PGW Results and Peak PWC Modeling Results Assuming Applications are Spreadout Based on the Breakthrough Time  
The x-axis shows the pesticide name followed by the ASM input half-life from shortest to longest duration.

### 5.3 Conclusions

In this section, a ground-truthing technique was carried out by parameterizing the model to replicate the conditions of the PGW study and to determine how changes to these parameters would provide results that are similar to or conservative in relation to those observed in the PGW studies. Generally speaking, it can be concluded that the standard modeling approach (30-years of application), along with increasing the zone of degradation or assuming a background degradation rate, produces EDWCs that are higher than those observed in the PGW studies.

When the PWC is parameterized to match the application scenario employed in the PGW study (*i.e.*, 1-year of applications), model estimated concentrations are higher than those observed in the PGW studies for all pesticides except for norflurazon, acifluorfen, and sulfentrazone, which were predicted to be lower than the maximum PGW concentration using the standard 1m0x assumption. Modeled concentrations that were lower than the PGW concentrations were within a factor of 10x the maximum PGW concentrations for the 1m0x, 2m0x, and 2m10x simulations. Additionally, there are reasons why the norflurazon, acifluorfen, and sulfentrazone PGW results might be different than those estimated using the PWC. There is not an obvious reason to explain the difference in measured and modeled concentrations for fenamiphos; however, the maximum PGW measured concentration of 0.58 µg/L was only slightly above the PWC predicted concentration of 0.14 µg/L with the 2m0x assumption<sup>m</sup>.

The pesticides that tended to be underpredicted degraded with a shorter half-life (47 days) and had a higher sorption coefficient ( $K_{oc} = 776 \text{ L/kg-oc}$ ). Consistent with previous evaluations, the PWC tends to predict low concentrations for pesticides with a short half-life and pesticides with a higher sorption coefficient which may be in the ASM degradation zone for a long period of time[ ADDIN EN.CITE ADDIN EN.CITE.DATA ].

While it is important not to underpredict exposure, it is also important not to overpredict exposure. Overpredictions of more than 10x occurred for four pesticides for the 1m0x and 1m10x assumptions, three pesticides with the 2m0x, 3m0x, 4m0x, 2m10x, 3m10x, and 4m10x assumptions. Changing the modeling assumptions resulted in more simulations with predicted concentrations within a factor of 10 of observed concentrations.

## 6 Water Quality Portal Monitoring Data Versus Modeling Results

Section [ REF\_Ref36382537 \r \h \\* MERGEFORMAT ] discusses the comparison of WQP [ ADDIN EN.CITE

<EndNote><Cite><Author>USEPA</Author><Year>2020</Year><RecNum>5276</RecNum><DisplayText><style face="superscript">56</style></DisplayText><record><rec-number>5276</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er"

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<sup>m</sup> Fenamiphos undergoes hydrolysis and there was not a 2m10x analysis for comparison.

timestamp="1560182365" guid="5de668aa-1ddd-4c19-b507-6aadebede625">5276</key></foreign-keys><ref-type name="Online Database">45</ref-type><contributors><authors><author>USEPA</author><author>USGS</author><author>NWQMC</author></authors></contributors><titles><title>Water Quality Portal</title></titles><dates><year>2020</year></dates><publisher>United States Environmental Protection Agency. United States Geological Survey. National Water Quality Monitoring Council</publisher><urls><related-urls><url>https://www.waterqualitydata.us/</url></related-urls></urls><access-date>March 23, 2018</access-date></record></Cite></EndNote>] monitoring data to PWC modeling results to better understand whether the different modeling assumptions would be reasonable and conservative across chemicals that vary in mobility and persistence.

The WQP database provides water monitoring data submitted by Federal, State, and local organizations including the National Water Quality Assessment (NAWQA) program. A more complete description of these data are available in previous reports [ ADDIN EN.CITE ADDIN EN.CITE.DATA ] and a brief description the NAWQA data is available in [ REF\_Ref36298914 \h \\* MERGEFORMAT ]. WQP data are collected from a variety of sources for various reasons. Samples may be from urban or agricultural wells, may not reflect areas vulnerable to GW leaching, may not be representative of drinking water wells, likely do not represent the conceptual model assumed in PWC modeling, and may not have been collected in an area where the pesticide was used. For these reasons, these ambient monitoring results may not capture the potential range of concentrations that may occur in the environment.

Ambient monitoring is not expected to result in similar EDWCs to those modeled because monitoring is collected at a variety of different sites that do not have characteristics like what we model. When comparing the modeled EDWCs to ambient monitoring concentrations, the monitoring may not have been collected in an area where the chemical is used or that is vulnerable to GW contamination. When modeled EDWCs exceed the ambient monitoring concentration, there is some confidence that we are being protective of what is expected to occur in the environment. When monitoring concentrations exceed the modeled EDWC, it is possible that the modeling may not be protective of concentrations that are occurring in GW or that the residues are due to a use pattern or site that is not reflected in the model simulation. When the monitoring concentration exceeds the modeled value, additional information on that result needs to be considered to determine if there is a reason that the modeled EDWC, that is supposed to reflect the high use scenario and a vulnerable site, does not exceed what we see in the natural environment. While we need to be protective, modeled EDWCs also need to be reasonable and reliable, so it is expected that some monitored GW concentrations will exceed modeled concentrations.

Peak PWC concentrations were compared to the maximum dissolved concentration reported as detected in groundwater in the WQP. The PWC estimates dissolved concentrations; therefore, total recovered WQP concentrations are not directly comparable to PWC dissolved concentrations. This maximum WQP concentration is utilized because it is uncertain what a

[ PAGE \\* MERGEFORMAT ]

percentile across sites with various sampling regimes and unknown vulnerabilities and usage history represents. When the PWC concentrations were exceeded by the monitoring results, the number of exceedances and the magnitude of the exceedances was further characterized.

For the PGW monitoring the modeled and measured concentrations are expected to be more similar, depending on how much the model simulation matched the GW monitoring analysis. The WQP comparison allows for an understanding of how the modeling is performing for a wider range of chemicals and conditions. In addition, it helps understand how the modeling and risk estimates relate to pesticides concentrations commonly observed in GW.

## 6.1 Methods

### 6.1.1 Monitoring Data Collection and Analysis

Pesticide selection for analysis is described in **Section 5**. Monitoring data were downloaded from the WQP in August 2018. Once downloaded, data were sorted for GW monitoring results and quality control samples, duplicates, and other values were removed. Units were converted to µg/L and sorted from highest to lowest. The peak value and mean of the highest five values were then summarized. For fifteen samples that were suspiciously “high” or modeled EDWCs exceeded the monitoring result, the source<sup>14</sup> of the data was consulted to determine whether the detection was due to a misuse, spill, and to make sure the sample reflected a reliable GW measurement. One sample reported for atrazine that exceeded the modeling results was identified to not be a reliable value (1400 µg/L collected on June 13, 1983)<sup>15</sup>, another field sample was determined to be mislabeled spiked sample. Additionally, a detection of chlorpyrifos at 458 µg/L was the result of a termiticide misuse<sup>16</sup>. Results without unreliable samples are described. A summary of the maximum WQP monitoring result is available in **Appendix E**.

### 6.1.2 Modeling

Modeling inputs were collected or calculated from the last drinking water assessment or ecological risk assessment using a provisional version of the PWC. These were placed in a batch input file and simulations were completed with the assumptions described previously.

Model inputs and monitoring results for each chemical simulated are available in **Appendix E**.

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<sup>14</sup> A range of sources were consulted based on information provided by the Water Quality Portal, including individuals from the organization who provided the data or reports associated with the reported endpoints. Finally, a list of samples was also shared with Bruce Lindsey with the USGS.

<sup>15</sup> Personal communication with Joseph Duris with the United States Geological Survey reviewed the sample and found it was likely a database error.

<sup>16</sup> Personal communication with Paul Buszka with the Ohio -Kentucky-Indiana Water Science Center on August 1, 2018.

6.2 Results

6.2.1 Comparison of 30-year simulation Versus 100-year simulation

Currently, when estimating concentrations in GW, the simulation is initially run for 30-years. When throughputs are less than one, the simulation is extended to 100-years. Once throughputs are greater than one, the concentrations in GW will remain relatively constant. When throughputs are less than one, concentrations will continue to increase over time. A “throughput” is the number of void volumes in the vadose zone that must be flushed through to get the main pulse of contaminant into the saturated zone. For a simulation with one application, this is the time right before the first peak of the concentration occurs. This does not indicate that it takes 100-years for the chemical to move into GW.

Standard EFED guidance is to model 30-year simulations. If breakthrough is not achieved (*i.e.*, throughput less than one in 30 years, a 100-year simulation is performed. Because the WQP pesticides evaluated have a range of properties some pesticides have throughputs greater than one in 30-years and some need to be simulated for 100-years. Following the standard recommendation would result with both 30-year simulations and 100-year simulations in the data analyzed. In [ REF\_Ref36372218 \h \\* MERGEFORMAT ] the estimated peak and post-breakthrough average pesticide concentration in GW for simulations that had throughputs greater than one for the 30-year simulation for the chemicals analyzed. It shows that once throughputs are greater than one, the EDWCs were similar for the 30-year and 100-year simulation. As the EDWCs for 30-year simulations and 100-year simulations were very similar, 100-year simulations were used for analysis and comparison to WQP monitoring results to avoid the need to combine different lengths of simulations in data analysis.

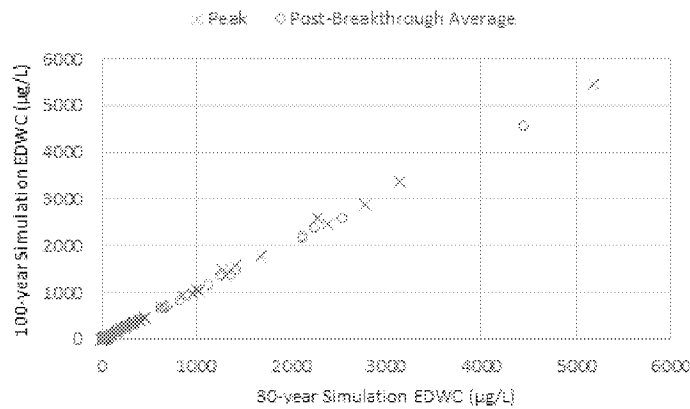


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Comparison of pesticide concentrations in groundwater simulated for 100-year and 30-years for chemicals with throughputs greater than one

## 6.2.2 Water Quality Portal Monitoring Versus Modeling for Pesticides with Breakthrough

The PWC predicts dissolved concentrations and thus, the recovered and total fractions are not directly comparable to the PWC result. Section [ REF\_Ref36382537 \r \h \\* MERGEFORMAT ] analysis was made by comparing only the samples with dissolved concentrations reported, as the recovered and total samples, may have some residues sorbed to filterable particles. Results considering all sample are summarized in [ REF\_Ref36384411 \h \\* MERGEFORMAT ].

[ REF\_Ref36384412 \h \\* MERGEFORMAT ] summarizes the comparison of the PWC modeling to the WQP portal monitoring maximum concentrations of dissolved sample fractions for each pesticide. Results are summarized by changes in the ASM zone assumptions where the analysis covered 54 chemicals. Results are also summarized for chemicals that are stable to hydrolysis and a background degradation rate is assumed as 10X the ASM half-life for 38 pesticides. Note that the maximum EDWC across six PWC scenarios is summarized in the section. Results would be different if a subset of PWC scenarios were considered.

When considering the impacts of increasing the zone of metabolism only ([ REF\_Ref36384412 \h \\* MERGEFORMAT ]a), PWC peak modeled concentrations were more than a factor of 10 lower than the WQP measured concentrations 9% of the time with the 1m0x assumption, which increases to 19% at the 4m0x assumption. The number of PWC peak modeled concentrations within a factor of 10x the WQP concentration increases from 22% using the 1m0x assumption to 31% with the 4m0x assumption. The number of PWC modeled concentration that are more than 10x higher than the maximum WQP concentration decreases from 69% with the 1m0x assumption to 50% at the 4m0x assumption.

Table [ STYLeref 1 \s ]-[ SEQ Table \\* ARABIC \s 1 ]. Comparison of the Peak Modeled Groundwater Concentrations to the Maximum Water Quality Portal Measured Concentration (Dissolved Samples)

(a) Zone of Aerobic Soil Metabolism

Zone of ASM	PWC is 'X' Compared to WQP Max; n=54 <sup>1,2</sup> Number of Pesticides (Percent of Pesticides)		
	X= More than 10x Higher	Within 10x Higher or Lower	More than 10x Lower
1m	37 (69%)	12 (22%)	5 (9%)
2m	32 (59%)	15 (28%)	7 (13%)
3m	28 (52%)	17 (31%)	9 (17%)
4m	27 (50%)	17 (31%)	10 (19%)

(b) Zone of Aerobic Soil Metabolism and Assuming the Hydrolysis Input is 10x ASM

Zone of ASM	Hydrolysis Assumption	PWC is 'X' Compared to WQP Max; n=38 <sup>1,2</sup> Number of Pesticides (Percent of Pesticides)		
		X= More than 10x Higher	Within 10x Higher or Lower	More than 10x Lower
1m	None	32 (59%)	5 (9%)	1 (2%)
2m	None	29 (54%)	7 (13%)	2 (4%)
3m	None	25 (46%)	10 (19%)	3 (6%)
4m	None	24 (44%)	11 (20%)	3 (6%)

[ PAGE \\* MERGEFORMAT ]

1m	10x ASM	30 (56%)	6 (11%)	2 (4%)
2m	10x ASM	26 (48%)	9 (17%)	3 (6%)
3m	10x ASM	25 (46%)	10 (19%)	3 (6%)
4m	10x ASM	24 (44%)	11 (20%)	3 (6%)

ASM=aerobic soil metabolism; n=number of pesticides analyzed

<sup>1</sup> In this column the number of chemicals (percent of chemicals) analyzed where the PWC modeled concentration was 'More than 10x Higher', 'Within 10x Higher or Lower', and 'More than 10x Lower' than the maximum WQP measured concentration is reported.

<sup>2</sup> Telone, chloropicrin, aminopyralid, imazaquin, and flutolanil did not have any dissolved samples in the WQP dataset.

[ REF\_Ref36451772 \h \\* MERGEFORMAT ] displays the maximum WQP dissolved pesticide concentration on the x-axis and the PWC peak pesticide concentration on the y-axis. Datapoints below the one to one line indicate that the PWC concentration was lower than the WQP measured concentrations. Datapoints between the one to one line and the first set of dashed lines above and below the one to one line are within a factor of 10x. The second dashed line represents datapoints that would be 100x above or below the one to one line. The graph in the upper left corner displays the results for the standard modeling assumption (1m0x) as a gray x. The graph in the upper right corner displays adds datapoints based on the 2m0x modeling assumption as an orange triangle. As the WQP maximum measured concentration is the same for across modeling assumptions, the amount of change in the different modeling assumptions may be observed by looking at the degree of change between the x and triangle that occur in the same vertical line. The lower panels add an additional datapoint for the 3m0x and 4m0x modeling assumptions. Some datapoints below 0.01 µg/L are not shown.

While the PWC modeled concentrations are not expected to be similar to the WQP maximum concentrations, it is informative to understand how the observed concentrations in the field compare to the PWC modeled concentrations. [ REF\_Ref36451772 \h \\* MERGEFORMAT ] shows that as you increase the zone of metabolism the PWC modeled concentrations are within a factor of ten of the WQP measured concentrations. The pesticides where PWC concentrations are more than 10x below the WQP maximum concentrations with concentrations above 0.01 µg/L increases from one datapoint with the 1m0x assumption to four pesticides with the 4m0x assumption.

When examining how assuming that the hydrolysis input is 10x the ASM input for chemicals that are stable to hydrolysis, the baseline to compare to for the standard analysis includes only 38 chemicals that were stable to hydrolysis ([ REF\_Ref36384412 \h \\* MERGEFORMAT ]b and [ REF\_Ref36461645 \h \\* MERGEFORMAT ]). PWC peak modeled concentrations were more than a factor of 10 lower than the WQP measured concentrations 2% to 6% of pesticides across modeling assumptions. The number of PWC peak modeled concentrations within a factor of 10x the WQP concentration increases from

- 9% using the 1m0x assumption to
- 11% using the 1m10x assumption, and
- 20% with the 4m10x assumption.

[ PAGE \\* MERGEFORMAT ]



The number of PWC modeled concentration that are more than 10x higher than the maximum WQP concentration decreases from

- 59% with the 1m0x assumption to
- 56% at the 1m10x assumption to
- 44% with the 4m10x assumption.

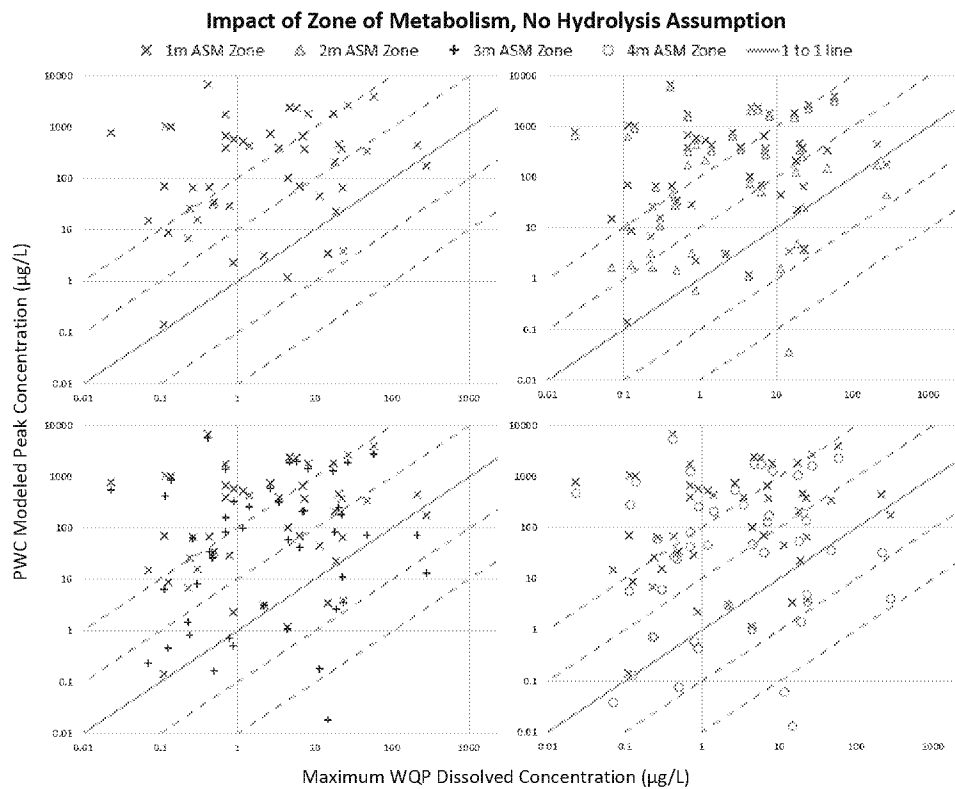


Figure [ STYLEREf 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Impact of Changing the Zone of Metabolism on the Comparison of the PWC Modeled Peak EDWCs to the Maximum Dissolved WQP Concentration

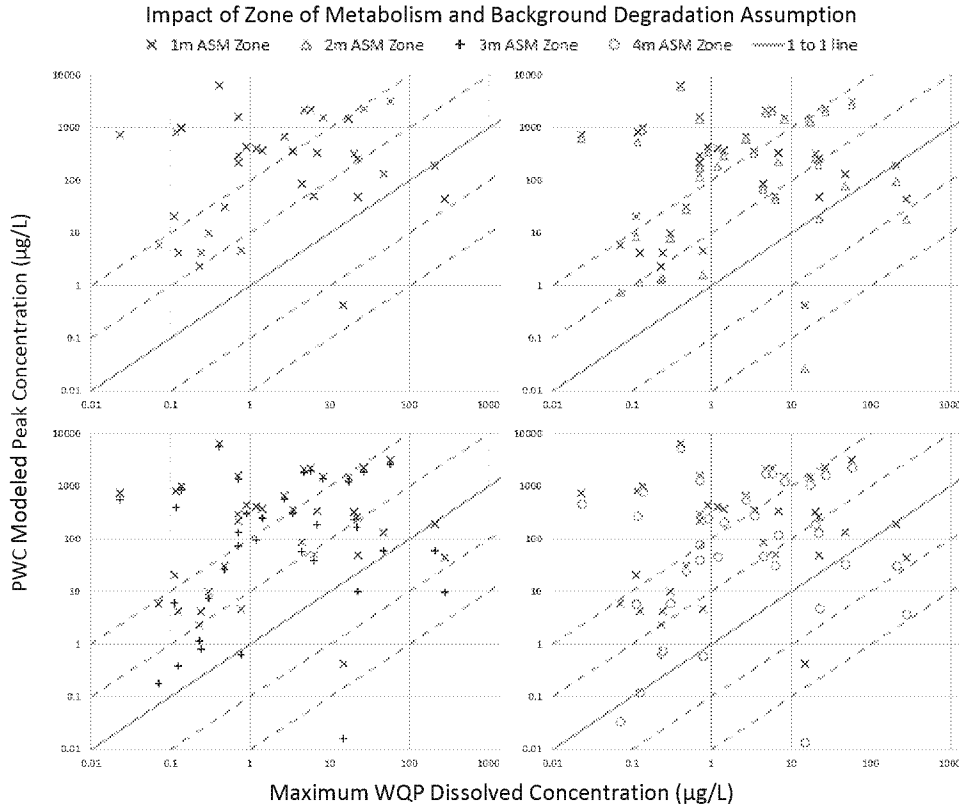


Figure [ STYLeref 1 \s ]-[ SEQ Figure \\* ARABIC \s 1 ]. Impact of Changing the Zone of Metabolism and Background Degradation Rate (10x ASM) on the Comparison of PWC Modeled Peak EDWCs Versus Maximum Dissolved Concentration from the WQP

[ REF\_Ref37240215 \h \\* MERGEFORMAT ] lists pesticide where WQP measured concentrations (considering all WQP samples) were higher than the PWC modeled concentration, along with the pesticide properties, and predicted and measured concentrations. Many of these chemicals were mobile or had half-life values (either ASM or hydrolysis) less than 45-days.

Table [ STYLEREf 1 \s ]-[ SEQ Table \\* ARABIC \s 1 ]. Summary of PWC Modeled Pesticide Concentrations and WQP Monitoring for Pesticide with PWC Modeling Lower than the Maximum WQP Measured Concentration

Pesticide	K <sub>oc</sub> (mL/g)	Half-life (days)		Highest Pesticide Concentration in Groundwater (µg/L)								Count Peak PWC Below WQP Dissolved*	
		Hydrolysis	Soil	Detections / Samples	WQP-Dissolved	1m0x	2m0x	3m0x	4m0x	1m10x	2m10x	1m0x	2m0x
Propanil	851	0	0.5	27 / 23,457	0.219	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	8	8
Azinphos-methyl	K <sub>d</sub> = 8.414	37	95	23 / 33,791	0.432	<0.01	<0.01	<0.01	<0.01	--	--	31	31
Terbufos	1448	15	81	14 / 26,695	0.36	<0.01	<0.01	<0.01	<0.01	--	--	11	11
Parathion-methyl	486	40	11	23 / 33,791	0.08	<0.01	<0.01	<0.01	<0.01	--	--	6	6
Disulfoton	552	300	20	19 / 25,498	0.109	0.14	<0.01	<0.01	<0.01	--	--	6	6
Bentazon	K <sub>d</sub> = 0.898	1197	48.9	580 / 15,689	11.5	45.4	<b>1.54</b>	<b>0.18</b>	<b>0.06</b>	--	--	0	18
2,4-D	K <sub>d</sub> = 0.52	0	6.92	425 / 26,306	14.8	<b>3.41</b>	<b>0.04</b>	<b>0.02</b>	<b>0.01</b>	<b>0.42</b>	<b>0.03</b>	0	19
Diazinon	758	138	123	97 / 35,241	19	22.4	<b>4.80</b>	<b>2.58</b>	<b>1.45</b>	--	--	0	3
Aldicarb	K <sub>d</sub> = 0.33	0	8.47	52 / 13,509	0.239	26.3	1.69	0.83	0.74	4.21	1.42	0	0
Glyphosate	157	0	29	138 / 1,783	280	<b>177</b>	<b>45.07</b>	<b>13.1</b>	<b>4.15</b>	<b>44.3</b>	<b>17.8</b>	2	3
Malathion	151	100	3	97 / 35,241	0.88	2.28	<b>0.57</b>	<b>0.50</b>	<b>0.43</b>	--	--	0	1
Cycloate	562	0	38.4	2 / 7,665	0.07	15.2	1.67	0.23	0.04	5.85	0.76	0	0
Iprodione	426	4.7	48	1 / 9,283	0.016	<0.01	<0.01	<0.01	<0.01	--	--	1	1
Acetochlor	133	0	13.3	529 / 34,007	0.77	29.2	3.24	<b>0.72</b>	<b>0.60</b>	4.65	1.60	0	0
Fenamiphos	K <sub>d</sub> = 0.958	300	47.1	423 / 14,104	0.497	33.6	1.47	<b>0.16</b>	<b>0.08</b>	--	--	0	0
Atrazine	75	0	139	14,410 / 51,027	20	464	334	2510	196.7	324	260	0	0
Carbofuran	30	28	321	341 / 38,097	2.16	3.14	3.10	3.08	3.06	--	--	0	0
Oxamyl	35	8	35	46 / 14,385	23	3.82	3.67	3.61	3.57	--	--	1	1
Metolachlor	181	0	49	5,376 / 48,273	210	443	<b>169</b>	<b>73.2</b>	<b>33.4</b>	<b>189.12</b>	<b>94.9</b>	0	1
Clopyralid	0.4	0	109	29 / 13,612	22.6	66.4	25.1	<b>11.0</b>	<b>5.03</b>	<b>48.8</b>	<b>18.8</b>	0	0
Carbaryl	211	12	176	274 / 44,585	4.42	<b>1.18</b>	<b>1.10</b>	<b>1.07</b>	<b>1.05</b>	--	--	3	3
Chloropicrin	36.05	0	0.9	11 / 2,294	--	35.2	0.35	0.23	0.17	0.59	0.31	--	--
Alachlor	86	0	42	3251 / 9592	8.8	343	148	71.83	36.17	131.37	78.40	0	0

WQP=Water Quality Portal

PWC EDWCs that were lower than the maximum WQP measured concentration are in bold. Pesticides are in order of the greatest to least underpredictions based on the 1m0x as compared to the WQP All result.

\* Number of WQP measured concentrations that were higher than the PWC modeled peak concentration.

When considering only the dissolved samples, the number of pesticides with WQP samples that were higher than PWC predicted concentrations ranged from 9 to 19 pesticides, depending on the modeling assumptions. Five of these pesticides (propanil, azinphos-methyl, terbufos, parathion-methyl, and disulfoton) had PWC modeled concentrations much less than 0.01 µg/L (all < 0.5 µg/L) due to rapid degradation of the pesticide. For these pesticides, any detection exceeded the PWC modeled concentrations. While these WQP detections were higher than the PWC modeling, the concentrations being measured in the field are also very low.

Excluding these five chemicals, seven and 50 total WQP dissolved samples were higher than PWC modeling using the 1m0x assumption and 2m0x assumption, with only one of those more than 10x lower the maximum WQP dissolved concentration. Most of the pesticides had more than 10,000 GW samples collected, the detection frequency was very low (less than 1%) with many of the detections near the detection limit for these pesticides. Assuming a 3m0x assumption results in three PWC modeled concentration more than 10x lower than the maximum WQP measured concentration; however, most of these have maximum WQP dissolved concentrations that are low (less than 0.5 µg/L). As observed in other analysis, the 3-m and 4-m zone of degradation results are relatively similar.

When evaluating the 10x ASM background degradation rate assumption, only three pesticides have a PWC peak GW concentration more than 10x lower than the maximum WQP dissolved concentration, even when assuming a 3-meter and 4-meter zone of degradation.

#### 6.2.3 Water Quality Portal Monitoring Data Versus Modeled Concentrations for Pesticides without Breakthrough

When considering results for pesticides with a  $K_{oc} > 1966$  L/kg-organic carbon with throughputs less than one (*i.e.*, those that did not achieve complete breakthrough), all PWC modeled EDWCs were lower than measured concentrations, even with a 100-year simulation ([**REF \_Ref45535342 \h \\* MERGEFORMAT**]). Movement of these pesticides is expected to be very slow, so detectable residues in GW are not expected unless the pesticide is very persistent. The measured concentrations of these pesticides may be due to mechanisms of transport not simulated in the PWC such as macropore transport.

The estimated PWC concentrations for these chemicals was less than 0.03 µg/L, except for chlorpyrifos, where the predicted concentration was 1.5 µg/L. Measured concentrations ranged from not detected to 63 µg/L. While the predicted concentrations were low, there were some detections of these chemicals in GW. Additional analysis on the reliability of these detections was not completed. If the maximum WQP detected concentrations are outliers, the mean of the top five WQP results<sup>17</sup>, are also higher than PWC EDWCs for these pesticides. This analysis demonstrates that chemicals with low mobility still have potential to move into GW.

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<sup>17</sup> These samples likely reflect detections from different sites with a range of vulnerability and use patterns.

Table [ STYLEREf 1 \s ]-[ SEQ Table \\* ARABIC \s 1 ]. Comparison of Modeling to Monitoring for Pesticides with Throughputs <1

Pesticide	Mean K <sub>oc</sub> (L/kg-oc)	Half-life (days) Input		Pesticide Concentration µg/L			
		Hydrolysis	ASM	Max WQP	Max WQP Dissolved	Mean of Top 5 WQP Dissolved	Max PWC 1m
Benfluralin	10750	0	75	0.406	0.406	0.10	0.0001
Chlorothalonil	4039	0	16	2.1	0.41	0.77	0.00005
Chlorpyrifos	6040	0	170.6	3.4 <sup>1</sup>	3.4	3.1	1.50
Cypermethrin	20800	210	219	0.335	0.335	0.172	0.00008
Dacthal	2627	0	60	63	Not available	53.6	0.06
Ethalfuralin	3957	0	48.5	0.09	0.09	0.04	0.008
Linuron	2000	1139	628	18	0.94	3.99	0.32
Pendimethalin	19768	0	172	0.824	0.824	0.33	0.00001
Propyzamide	1966	0	43.7	Not Detected			1.2E-09
Trifluralin	8758	375	314	1	0.15	0.7	0.04

ASM=Aerobic soil metabolism; WQP=Water Quality Portal; PWC=pesticide in water calculator

1. A detection of chlorpyrifos at 458 µg/L was the result of a termiticide misuse and reflects total recoverable fraction and was not included in the table.

### 6.3 Conclusions

Overall, these results show that the PWC modeled concentrations assuming a 1-meter zone of degradation assumption results in EDWCs higher than the maximum measured dissolved WQP concentrations for approximately 90% of pesticides evaluated. Increasing the zone of degradation increased the number of PWC modeled EDWCs lower than WQP maximum measured concentrations but most PWC EDWCs were still within 10x the WQP measured concentration. Less than 19% of pesticides had PWC predicted concentrations greater than 10x lower the maximum WQP measured result across all modeling assumptions.

Assuming a background degradation half-life of 10x the ASM was also conservative for 76 to 92% pesticides when considering the dissolved phase concentrations only, even when combining the 10x assumption with the zone of degradation modifications. PWC modeling has a tendency to underpredict concentrations of pesticides that degrade with half-life values of less than 40-days and for some pesticides that are not mobile (K<sub>oc</sub> values range from 2000 to 19,768 L/kg-oc). Measured concentrations for these chemicals occur but tend to be at low concentrations (<1 µg/L). These conclusions are consistent with those from previous analyses of the PWC results.

## 7 Summary

The work presented in this report was intended to increase the ability of PWC users to consider subsurface metabolism in estimating pesticide concentrations in GW using the PWC. This included a literature review of metabolic activity of pesticides in subsurface soils, and the

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exploration of alternative approaches to estimating metabolic activity in the soil profile using the PWC model. The main approaches for considering subsurface metabolism in modeling included (1) increasing the depth at which metabolic activity in PWC ceased, 1 meter, to some greater depth, (2) assuming a background degradation rate in the dissolved phase based on the ASM half-life while holding the depth at 1.0 meter, and (3) items 1 and 2 combined. While a range of assumptions for increasing the zone of metabolism were explored (up to 4-meters), much of the analysis focused more heavily on the results considering a 2-meter zone of metabolism because very limited data are available examining subsurface metabolism below 2-meters.

In general, we have found that degradation rates decline with depth; however, degradation other than hydrolysis<sup>18</sup> did occur at a slow rate, even at depths below 2-meters for some soils and pesticides. Open literature data support exploring modeling results with changes in the ASM metabolism zone and assuming a background degradation rate. When considering modeling assumptions an increase in metabolic depth reduced EDWC more than the use of a subsurface background rate (dissolved phase) set at 1/10 of the surface aerobic metabolism rate.

When the PWC is parameterized to match the application scenario employed in the PGW study (*i.e.*, 1-year of applications), model estimated concentrations are higher than those observed in the PGW studies for all pesticides except for norflurazon, acifluorfen, and sulfentrazone, which were predicted to be lower than the maximum PGW concentration using the standard 1m0x assumption. More careful analysis of the PGW studies and modeling indicated there were reasons why the PWC estimates were lower than the observed concentrations. Modeled concentrations that were lower than the PGW concentrations were within a factor of 10x the maximum PGW concentrations for the 1m0x, 2m0x, and 2m10x simulations. Modeled concentrations were within 10x the maximum concentration observed in the PGW studies for more pesticides using the 2m0x and 2m10x as compared to the 1m0x assumption. EDWCs using the 1/10 of ASM half-life (1m10x) background modeling assumption were similar to the 2-meter zone of metabolism assumption, except for pesticides with a lower mobility (Koc value >500 L/kg-oc).

Comparison of the 2m0x and 1m10x modifications of PWC to ambient monitoring data from the WQP monitoring also indicates that PWC EDWCs are generally higher than the WQP measured concentrations. The number of PWC peak modeled concentrations within a factor of 10x the WQP concentration increases with increasing the zone of metabolism from 22% using the 1m0x assumption to 31% with the 4m0x assumption. The number of PWC peak modeled concentrations within a factor of 10x the WQP concentration also increases when assuming a background degradation rate (1/10 the ASM rate) from 11% using the 1m10x assumption to

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<sup>18</sup> The assumption that degradation other than hydrolysis is occurring is based on a 30-day hydrolysis study showing limited degradation for the chemical. A longer duration hydrolysis study may have shown that some hydrolysis would occur for the pesticide.

20% with the 4m10x assumption. Overall , less than 19% of pesticides had PWC predicted concentrations greater than 10x lower the maximum WQP measured result across all modeling assumptions. For the pesticides where the PWC EDWCs was lower than the WQP maximum measured concentration, often the concentrations observed were generally low (<0.5 µg/L and for a small number of samples.

PWC modeling has a tendency to underpredict concentrations of pesticides that degrade with half-life values of less than 47-days and for some pesticides that are not mobile ( $K_{oc}$  values range from 2000 to 19,768 L/kg-oc). Measured concentrations for these chemicals occur but tend to be at low concentrations (<1 µg/L). These conclusions are consistent with those from previous analyses of the PWC results. These pesticides are also less likely to leach into GW and persist for long periods.

In general, moving forward with increasing the zone of metabolism to 2-meters results in predicted concentrations that are within 10x observed concentrations. Further expansion of the metabolism zone to 3- or 4-meters results in less-conservative EDWCs versus monitoring data and fewer datapoints are available examining degradation in the subsurface. Open literature data indicated that the subsurface metabolism half-life was less than 10x the surface metabolism half-life for 82% of datapoints available below 1-meter and 71% of datapoints below 2-meters. Thus, it is possible that for some chemicals that do not degrade quickly and are stable to hydrolysis a background degradation half-life may be considered in modeling. However, the data available examining degradation in the subsurface below 2-meters is limited to 17 datapoints from five studies. Very different results could be observed if a more robust dataset was available. The PWC predicted concentrations for pesticides that degrade with half-life values less than 47-days or that have high sorption coefficients ( $K_{oc} > 2500$  L/kg-oc) may be lower than the maximum concentrations detected in monitoring data.

## 8 Literature Cited

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# Appendix [SEQ Appendix \\* ALPHABETIC\s 1]. Surface and Subsurface Data Summary of Open Literature

In **Table A1** and **Table A2**, open literature studies containing paired surface- and subsurface-studies are summarized. Data were collected based on criterion listed in **Section [ REF\_Ref33607284 \r \h \\* MERGEFORMAT ]** (Open Literature Analysis). The collected data are organized in two categories:

1. Chemicals that Undergo Hydrolysis (**Table A1**);
2. Chemicals Stable to Hydrolysis (**Table A2**).

Surface and subsurface half-life data, along with soil characteristics, were recorded from these studies. Tabulation varied between studies according to what authors reported, but commonly included pH, organic carbon concentration and unsaturated vs saturated subsurface conditions. The data are listed by pesticide and the reference in which the corresponding data were collected.

**Table A1. Half-life Data Summary for Chemicals That Undergo Hydrolysis**

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
3,5,6-Trichloro-2-Pyridinol	Baskaran et al., 2003 [ ADDIN EN.CITE <EndNote ><Cite><A uthor>Bas karan</A uthor><Yea r>2003</Y ear><Rec Num>394 9</RecNu m><Displa yText><st	49.0	72	0-15	15-30	Urrbrae soil	2.3	1.2-1.8	6.51	6.02-6.6	SFO
			117		45-90			0.6-0.9		7.17-7.7	
		42.0	64	0-15	15-30	Wiesenboden soil	2.9	1.4-2.0	6.6	6.25-7.04	
			94		45-90			0.5-1.0		7.75-7.96	



Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	key></for eign- keys><ref- type name="Jo urnal Article">1 7</ref- type><con tributors> <authors> <author>B askaran, S.</autho r><author >Kookana, R. S.</autho r><author >Naidu, R.</autho r></autho rs></contr ibutors><t itles><title >Contrasti ng behaviour of chlorpyrif os and its primary metabolit e, TCP										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	(3,5,6-trichloro-2-pyridinol), with depth in soil profiles</title><secondary-title>Australian Journal of Soil Research</secondary-title></titles><periodical><full-title>Australian Journal of Soil Research</full-title></periodical><pages>749-760</pages><volume>41</v										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	<p>           olume&gt;&lt;n            umber&gt;4&lt;            /number&gt;            &lt;dates&gt;&lt;y            ear&gt;2003            &lt;/year&gt;&lt;p            ub-            dates&gt;&lt;da            te&gt;2003&lt;/            date&gt;&lt;/pu            b-            dates&gt;&lt;/d            ates&gt;&lt;isb            n&gt;0004-            9573&lt;/isb            n&gt;&lt;access            ion-            num&gt;WO            S:0001842            75500012            &lt;/accessio            n-            num&gt;&lt;url            s&gt;&lt;related            -            uris&gt;&lt;url&gt;            &amp;lt;Go to            ISI&amp;gt;://            WOS:0001            84275500            012&lt;/url&gt;            &lt;url&gt;http:            //www.pu            blish.csiro         </p>										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	.au/sr/SRO2062</url></related-urls></url>s><electronic-resource-num>10.1071/sr02062</electronic-resource-num></record></Cite></EndNote>]										
Carbaryl	Nkedi-Kizza and Brown, 1998 [ADDIN EN.CITE<EndNote><Cite><Author>Nkedi-Kizza</Author><Year>1998</Year><RecNum>5315</RecNum><Displa	9.0	18	0-30	31-60	Red Bay soil	15.2	3.9	6.3	5.3	
		8.0	13	0-30	31-60	Asatulta soil	8	2	5.6	4.8	

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Chlorpyrifos	Baskaran <i>et al.</i> , 2003 [ADDIN EN.CITE <EndNote><Cite><Author>Bas	28	16	0-15	15-45	Urrbrae soil	2.3	1.2-1.8	6.51	6.02-6.6	
			10		45-90			0.6-0.9		7.17-7.7	
		23	13	0-15	15-45	Wiesenboden soil	2.9	1.4-2.0	6.6	6.25-7.04	
			7		45-90			0.5-1.0		7.75-7.96	

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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	Sirisha <i>et al.</i> 2006 [ADDIN EN.CITE <EndNote><Cite><Author>Sirisha</Author><Year>2006</Year><RecNum>3730</RecNum><DisplayText><style face="superscript">36</style></DisplayText><record><rec-number>3730</rec-number><foreign-	10.6	33.5	0-15	40-50	10 ug/g	0.9	0.4	7.4	7.3	
		20.6	154		40-50	100 ug/g	0.9	0.4	7.4	7.3	
		154	385		40-50	1000 ug/g	0.9	0.4	7.4	7.3	

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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	e></EndNote>]										
cis-1,3-Dichloro propene	Ou <i>et al.</i> 1995 [ ADDIN EN.CITE <EndNote ><Cite><A uthor>Ou </Author> <Year>19 95</Year> <RecNum >4474</R ecNum>< DisplayT ext><style face="sup erscript"> 37</style> </DisplayT ext><reco rd><rec- number>4 474</rec- number>< foreign- keys><key app="EN" db- id="s0xer 2w2o0xw x3e0a0tx0 sz3zradtt	20	18	0-15	15-30	Gainesville, FL- Ellzey fine sand <sup>3</sup>	N/A	N/A	N/A	N/A	
		8	11	0-15	15-30	Gainesville, FL- Ellzey fine sand	N/A	N/A	N/A	N/A	

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Deethylatrazine	Kruger <i>et al.</i> 1997[ ADDIN EN.CITE <EndNote><Cite><Author>Kruger</Author><Year>1997</Year><RecNum>4401</RecNum><DisplayText><style face="superscript">25</style></DisplayText><record><record-number>4401</record-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xw	33	182	0-30	90-120	Nonsterile Soil	2.6	0.6	5.7	6.2	

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	J.</author>><author> Anhalt, J. C.</author>r><author> Anderso n, T. A.</author>r><author> Coats, J. R.</author>r></author>rs></contr ibutors><t itles><title> >Compara tive fates of atrazine and deethylatr azine in sterile and nonsterile soils</title>><second ary- title>Jour nal of Environm ental Quality</s econdary- title></titl										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation	
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface		
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Diazinon	Sarmah <i>et al.</i> 2009 [ADDIN EN.CITE<EndNote><Cite><Author>Sarmah</Author><Year>2009</Year><RecNum>5316</RecNum><DisplayText>st	7	8	0-10	40-50	Waikiwi silt loam 20C	3.9	0.87	5.5	6.7	Graphical <sup>2</sup>	
		8	25			Waikiwi silt loam, 7.5 C						
		5	24			Motupiko silt loam 20C	2.4	0.26	5.7	6.1		
		12	12			Motupiko silt loam, 7.5C						

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	urnal Article">1 7</ref- type><con tributors> <authors> <author>S armah, Ajit K.</autho r><author >Close, Murray E.</autho r><author >Mason, Norman W. H.</autho r></autho rs></contr ibutors><t itles><title >Dissipati on and sorption of six commonly used pesticides in two contrastin g soils of New										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	080/0360 12309028 00960</el ectronic- resource- num></re cord></Cit e></EndN ote>]										
Fenamiphos	Di <i>et al.</i> , 1998 [ ADDIN EN.CITE <EndNote ><Cite><A uthor>Di< /Author>< Year>199 8</Year>< RecNum> 4314</Re cNum><Di splayText ><style face="sup erscript"> 35</style> </DisplayT ext><reco rd><rec- number>4 314</rec- number>< foreign-	24	72	0-25	25-50	Sandy soil	0.53	0.15	5.3	5.5	SFO

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	<author> Di, H. J.</author> ><author> Aylmore, L. A. G.</autho r><autho r><autho r></contr ibutors><t itles><titl e>Degradat ion rates of eight pesticides in surface and subsurfac e soils under laboratory and field conditions </title><s econdary- title>Soil Science</ secondary - title></titl										



Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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	Kookana <i>et al.</i> , 1997 [ ADDIN EN.CITE <EndNote ><Cite><A uthor>Ko	1.4	34.7	0-25	25-50	Bassendean soils	0.53	0.02	5.3	5.5	Graphical <sup>2</sup>

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	okana</A uthor><Ye ar>1997</ Year><Rec Num>525 1</RecNu m><Displa yText><st yle face="sup erscript"> 63</style> </DisplayT ext><reco rd><rec- number>5 251</rec- number>< foreign- keys><key app="EN" db- id="s0xer 2w2o0xw x3e0a0tx0 sz3zradtt w529er" timestam p="15818 91392" guid="8fe 95e7e- 41d8- 431b-										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Fenamiphos Sulfone	Chung and Ou, 1996 [ADDIN EN.CITE <EndNote><Cite><Author>Chung</Author><Year>1996</Year><RecNum>4429</RecNum><DisplayText><style face="superscript">38</style></DisplayText><record><record-number>4429</record-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xw	1.0	2.7	0-15	15-30	Fairway, turfgrass	2.13	0.33	6.8	6.6	SFO
		8.4	12.4			Rough, turfgrass	1.35	0.61	7.6	7.1	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Fenamiphos sulfoxide total residues	Chung and Ou, 1996 [ADDIN EN.CITE <EndNote ><Cite><Author>Chung</Author><Year>1996</Year><Rec	2.7	3.1	0-15	15-30	Fairway, turfgrass	2.13	0.33	6.8	6.6	SFO
		20.5	30.2			Rough, turfgrass	1.35	0.61	7.6	7.1	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Fenamiphos total residue	Kookana <i>et al.</i> , 1997 [ ADDIN EN.CITE <EndNote ><Cite><Author>Kookana</Author><Year>1997</Year><RecordNum>5251</RecordNum><DisplayText><style face="superscript">63</style></DisplayText><record><record-number>5251</record-number><	50	140	0-25	25-50	Bassendean soils	0.53	0.02	5.3	5.5	Graphical <sup>2</sup>

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	Phang, C. Aylmore, L. A. G. Transformation and degradation of fenamiphos nematicide and its metabolites in soils<second ary-title>Soil Research</secondar y-title></titl es><perio dical><full -title>Soil Research<										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation	
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Hexazinone	Sarmah <i>et al.</i> , 2009 [ADDIN EN.CITE<EndNote><Cite><Author>Sarmah</Author><Year>2009</Year><RecNum>5316</RecNum><DisplayText><style face="sup	8	92	0-10	40-50	Waikiwi silt loam, 7.5C	3.9	0.87	5.5	6.7	Graphical <sup>2</sup>	
		36	68			Waikiwi silt loam. 20C						
		45	55			Motupiko silt loam 20C	2.4	0.26	5.7	6.1		
		96	140			Motupiko silt loam 7.5C						

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	00960</el ectronic- resource- num></re cord></Cit e></EndN ote>]										
Imidacloprid	Leiva <i>et al.</i> , 2015 [ADDIN EN.CITE <EndNote><Cite><Author>Leiva</Author><Year>2015</Year><RecNum>5317</RecNum><DisplayText><style face="superscript">64</style></DisplayText><record><rec-number>5317</rec-number><foreign-keys><key app="EN"	511	686	0-15	15-30	Immokalee fine sand	0.1	0.003	4.4	4.5	zero-order
			948		30-45		0.1	0.002	4.4	4.4	
			440		45-60		0.1	0.02	4.4	4.4	
			359		60-75		0.1	0.03	4.4	4.6	

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	es><periodical><full title>Journal of Agricultural and Food Chemistry</full-title></periodical><pages>4915-4921</pages><volume>63</volume><number>20</number><dates><year>2015</year><pub-dates><date>2015/05/27</date></pub-dates></dates><publisher>American Chemical Society</p										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	ublisher>< isbn>0021 - 8561</isbn><urls>< related-urls><url> https://doi.org/10.1021/acs.jafc.5b00532</url></related-urls></url><electronic-resource-num>10.1021/acs.jafc.5b00532</electronic-resource-num></record></Cite></EndNote>]										
Linuron	Di et al., 1998 [ ADDIN EN.CITE <EndNote ><Cite><Author>Di<	142.0	88.0	0-25	25-50	Sandy soil	0.53	0.15	5.3	5.5	SFO

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	ion rates of eight pesticides in surface and subsurface soils under laboratory and field conditions										



Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	year>1998 </year><p ub- dates><da te>May</ date></pu b- dates></d ates><isb n>0038- 075X</isb n><access ion- num>WO S:0000738 18400008 </accessio n- num><url s><related - urls><url> &lt;Go to ISI&gt;:// WOS:0000 73818400 008</url> </related- urls></url s><electro nic- resource- num>10.1 097/0001										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	0694-199805000-00008</electronic-resource-number></record></Cite></EndNote>]										
Metribuzin	Webb and Aylmore, 2002 [ADDIN EN.CITE<EndNote><Cite><Author>Webb</Author><Year>2002</Year><RecNum>4061</RecNum><DisplayText><style face="superscript">47</style></DisplayText><record><rec-number>4	145	222								
		212	193	0-25	25-50	Karrakatta sand	1.1	0.14	5.5	5.4	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	type><con tributors> <authors> <author> Webb, K. M.</auth or><autho r>Aylmore , L. A. G.</autho r></autho rs><secon dary- authors>< author>Vi olante, A.</autho r><author >Huang, P. M.</auth or><autho r>Bollag, J. M.</auth or><autho r>Gianfre da, L.</author ></second ary- authors>< /contribut ors><titles										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	><title>The role of soil organic matter and water potential in determining pesticide degradation</title> <secondary- title>Soil Mineral-Organic Matter-Microorganism Interactions and Ecosystem Health, Vol 28a: Dynamics, Mobility and Transformation of Pollutants and Nutrients										

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	ISI&gt;://WOS:000177766900008</url></related-urls></url>s></record></Cite></EndNote>]										
	Di <i>et al.</i> , 1998 [ADDIN EN.CITE<EndNote><Cite><Author>Di</Author><Year>1998</Year><RecNum>4314</RecNum><DisplayText><style face="superscript">35</style></DisplayText><record><rec-number>4314</rec-number><	46	77			Sandy soil	0.53	0.15	5.3	5.5	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	<authors> <author> Di, H. J.</author> ><author> Aylmore, L. A. G.</author> r><author> >Kookana, R. S.</author> r></author> rs></contr ibutors><t itles><title> >Degradat ion rates of eight pesticides in surface and subsurfac e soils under laboratory and field conditions </title><s econdary- title>Soil Science</ secondary -										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	n- num><url s><related - urls><url> &lt;Go to ISI&gt;;// WOS:0000 73818400 008</url> </related- urls></url s><electro nic- resource- num>10.1 097/0001 0694- 19980500 0- 00008</el ectronic- resource- num></re cord></Cit e></EndN ote>]										
	Henriksen et al., 2004 [ ADDIN EN.CITE <EndNote ><Cite><A	32	>500		300-400	sandy soil	0.85	0.1	5.5	5.98	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	Metribuzin and Primary Metabolites in a Sandy Soil</title><secondary-title>Journal of Environmental Quality</secondary-title></titles><periodical><full-title>Journal of Environmental Quality</full-title></periodical><pages>619-627</pages><volumes>33</volumes><number>2<										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	/number> <dates><year>2004</year></dates><urls><related- - urls><url> http://dx. doi.org/10 .2134/jeq 2004.6190 </uri></re lated- urls></url s><electro nic- resource- num>10.2 134/jeq20 04.6190</ electronic- resource- num><lan guage>En glish</lan guage></r ecord></C ite></End Note>]										
Procymidone	Sarmah et al., 2009 [ADDIN EN.CITE	37.0	48.0		40-50	Motupiko silt loam 20C	2.4	0.26	5.7	6.1	Graphical <sup>2</sup>

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	i.org/10.1080/03601230902800960</url></related-urls></url><electronic-resource-num>10.1080/03601230902800960</electronic-resource-num></record></Cite></EndNote>]										
Saflufenacil	Papiernik et al., 2012 [ADDIN EN.CITE<EndNote><Cite><Author>Papiernik</Author><Year>2012</Year><RecNum>5319</RecNum>	13	32	0-10	15-30	Minnesota prairie shoulder 15-30cm <sup>1</sup>	2.5	1.4	7.9	8	SFO
					45-60	Minnesota prairie shoulder 45-60cm <sup>1</sup>	2.5	1.2	7.9	8.1	
				0-15	15-30	Minnesota prairie footslope 15-30cm <sup>1</sup>	3.6	3.2	7.8	7.7	
					45-60	Minnesota prairie footslope 45-60cm <sup>1</sup>	3.6	0.8	7.8	7.9	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	type name="Jo urnal Article">1 7</ref- type><con tributors> <authors> <author>P apiernik, Sharon K.</autho r><author >Koskinen , William C.</autho r><author >Barber, Brian L.</author ></author s></contri butors><ti tles><title >Low Sorption and Fast Dissipatio n of the Herbicide Saflufenac il in Surface Soils and										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	Subsoils of an Eroded Prairie Landscape </title><secondary-title>Journal of Agricultural and Food Chemistry</secondary-title></titles><periodical><full-title>Journal of Agricultural and Food Chemistry</full-title></periodical><pages>10936-10941</pages><volume>60</volume><										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	021/jf303271p</electronic-resource-num></record></Cite></EndNote>]										
Sulfosulfuron	Sondhia and Singhai, 2008 [ADDIN EN.CITE<EndNote><Cite><Author>Sondhia</Author><Year>2008</Year><RecNum>5320</RecNum><DisplayText><style face="superscript">67</style></DisplayText><record><rec-number>5320</rec-	16.96	18.16	0-15	15-30	Soil from wheat field, 25 g ai/ha	0.8	0.78	7.2	7.1	
		17.88	19.55			wheat field, 50 g ai/ha dose	0.8	0.78	7.2	7.1	
		16.5	18.61			wheat field, 100 g ai/ha dose	0.8	0.78	7.2	7.1	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	author><a uthor>Sin ghai, Benu</aut hor></aut hors></co ntributors ><titles>< title>Persi stence of Sulfosulfu ron Under Wheat Cropping System</t itle><seco ndary- title>Bulle tin of Environm ental Contamin ation and Toxicology </seconda ry- title></titl es><perio dical><full - title>Bulle tin of Environm ental										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Thifensulfuron	McDowell et al., 1997 [ ADDIN EN.CITE <EndNote ><Cite><Author>McDowell</Author><Year>1997</Year><RecNum>5321</RecNum><DisplayText><style	5.4	6.4	0-15	15-20	Templeton silt loam 15C	5.73	4.13	5.42	5.51	NR

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	.wiley.com/doi/abs/10.1046/j.1365-3180.1997.d01-73.x</url></related-urls></url>s><electronic-resource-num>10.1046/j.1365-3180.1997.d01-73.x</electronic-resource-num></record></Cite></EndNote>]										
trans-1,3-Dichloro propene	Ou <i>et al.</i> , 1995 [ADDIN EN.CITE<EndNote><Cite><Author>Ou</Author><Year>1995</Year>	17	17	0-15	15-30	Gainesville, FL-Ellzey fine sand <sup>3</sup>	NR	NR	NR	NR	SFO
		3.0	4.0			Gainesville, FL-Ellzey fine sand <sup>4</sup>	NR	NR	NR	NR	

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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
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[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	or></auth ors></con tributors> <titles><ti tle>Degra dation of 1,3- Dichloropr opene (1,3-D) in Soils with Different Histories of Field Applicatio ns of 1,3- D</title>< secondary - title>Jour nal of Nematolo gy</secon dary- title></titl es><perio dical><full - title>Jour nal of Nematolo gy</full- title></pe riodical><										

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	<p>pages&gt;249-257&lt;/pages&gt;&lt;volume&gt;27&lt;/volume&gt;&lt;number&gt;3&lt;/number&gt;&lt;dates&gt;&lt;year&gt;1995&lt;/year&gt;&lt;pubdates&gt;&lt;date&gt;Sep&lt;/date&gt;&lt;/pubdates&gt;&lt;/dates&gt;&lt;isbn&gt;0022-300X&lt;/isbn&gt;&lt;accession-num&gt;WOS:A1995TD63500001&lt;/accession-num&gt;&lt;url&gt;&lt;related-urls&gt;&lt;url&gt;&lt;style face="underline"</p>										

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT <sub>50</sub> or T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	font="default" size="100 %">&lt;Go to ISI&gt;://WOS:A1995TD63500001</style></url><url>https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2619622/pdf/249.pdf</url></related-urls></records></Cite></EndNote>]										

NR=not reported; OC=organic carbon; NOM=natural organic matter; DT50=time to 50% loss; FOMC= Gustafson and Holden Model; SFO=single-first order;

DFOP=double first order in parallel

1 one regression for all subsurface data but properties were different at different depths.

2 Not described well with single first order equation

3 Untreated soil

[ PAGE \\* MERGEFORMAT ]

Table A2. Half-life Data Summary for Chemicals Stable to Hydrolysis

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
Acetochlor	Vaughn et al., 1999 <sup>21</sup>	18	8	0-30	30-76	Field- sandy loam, loamy sand	1.9	0.7-0.9	6.1	6.7-6.8	FOMC
			14		260-305	Field- sandy loam, sand		0.5-0.9		6.0-6.4	
		15	4.0	0-30	30-76	Laboratory, 20C, sandy loam, loamy sand	1.9	0.7-0.9	6.1	6.7-6.8	
			32.0		270-280	Laboratory, 20C, sandy loam, sand		0.5-0.9		6.0-6.4	
		8.0	2.0	0-30	30-76	Laboratory, field temp and moisture- sandy loam, loamy sand	1.9	0.7-0.9	6.1	6.7-6.8	
								0.5-0.9		6.0-6.4	
		8.0	10	0-30	270-280	Laboratory, field temp and moisture- sandy loam, sand	1.9	0.7-0.9	6.1	6.7-6.8	
								0.5-0.9		6.0-6.4	
	Bedmar et al., 2017[ ADDIN EN.CITE <EndNote><Cite>< Author>Bedmar</ Author><Year>2017</Year><RecNum>5322</RecNum>< DisplayText><style face="superscript">69</style></Displ	14.6	27.2	0-5	5-41	Topsoil General Alvarado Typic Argiudolls, Necochea series	7.48	5.16	5.8	5.85	SFO
			28.6		41-81			2.24		6.65	
			60.3		81-130			0.43		7.25	
		23.6	27.4	0-5	5-26	Topsoil Tres Arroyos Typic Argiudolls, Tres Arroyos series	3.44	2.92	5.5	5.8	
			40.8		26-51			2.06		6.05	
			72.9		51-110			0.52		6.45	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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[ PAGE \\* MERGEFORMAT ]



Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	metolachlor in surface and subsurface horizons of 2 typic argiudolls under no-tillage</title></titles><pages>3065-3073</pages><volume>36</volume><number>11</number><dates><year>2017</year></dates><isbn>0730-7268</isbn><urls><related-urls><url>https://setac.onlinelibrary.wiley.com/doi/abs/10.1002/etc.3874</url></related-urls></urls><electronic-resource-num>10.1002/etc.3874</electronic-resource-num></record></Cite></EndNote>]										
	Oliveira et al., 2013 [ ADDIN EN.CITE <EndNote><Cite><Author>Oliveira</Author><Year>2013</Year><RecNum	6.5	26.7	0-15	60-90	T1-09 site; soil pred. Waldorf <sup>1</sup>	6	1.4	8.1	7.6	DFOP
		13.5	20.3	0-15	60-90	T4-17 site; soil pred. Waldorf <sup>1</sup>	5.9	6.8	5.9	6.8	
		9.98	23.5	0-15	60-90	T6-01 site; soil pred. Waldorf <sup>1</sup>	9.7	8	7.7	7.8	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	J.</author><author>Nater, Edward A.</author><author>Alonso, Diego G.</author></authors></contributors><titles><title>Ace tochlor Persistence in Surface and Subsurface Soil Samples</title><secondary-title>Water, Air, & Soil Pollution</secondary-title></titles><periodical><full-title>Water, Air, & Soil Pollution</full-title></periodical><pages>1747</pages><volume>224</volume><number>10</number><dates><year>2013</year><pub-dates><date>2013/09/19</date></pub-dates></dates><isbn>1573-2932</isbn></url>										

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Acifluorfen	[ ADDIN EN.CITE <EndNote><Cite><Author>Gaston</Author><Year>2000</Year><RecNum>4214</RecNum><DisplayText><style face="superscript">20</style></DisplayText><record><rec-number>4214</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradtw529er" timestamp="1522175373" guid="be1afca1-	74.0	169	0-10	20-30	Conventional Till- silt clay loam, Aeris Ochraqualk	0.87	0.49	5.79	5.80	SFO
		108	165	0-10	20-30	No Till- silt clay loam, Aeris Ochraqualk	1.02	0.44	5.60	5.71	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	121</pages><volume>64</volume><number>1</number><dates><year>2000</year><pubdates><date>Jan-Feb</date></pubdates></dates><isbn>0361-5995</isbn><accession-num>WOS:000089446000014</accession-num><urls><related-urls><url>&lt;Go to ISI&gt;://WOS:000089446000014</url></related-urls></urls></record></Cite></EndNote>]Gaston and Locke, 2000 [ADDIN EN.CITE<EndNote><Cite><Author>Gaston</Author><Year>2000</Year><RecNum>4214</RecNum><DisplayText><style face="superscript">20</style></DisplayText><record><r										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
Alachlor	Stolpe & Shea, 1995 [ ADDIN EN.CITE <EndNote><Cite><Author>Stolpe</Author><Year>1995</Year><RecNum>4557</RecNum><DisplayText><style face="superscript">21</style></DisplayText><record><record-number>4557</record-number><foreign-keys><key app="EN" db-id="s0xer2w2o0wx3e0a0tx0sz3zradtw529er" timestamp="1522175453" guid="82290186-eb19-42cc-add2-b8cc1bd068ed">4557</key><key app="ENWeb" db-id="">0</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author	9.0	21	0-15	45-120	North Site	1.02	0.33	7.6	7.9	
			19		150-240			0.02		8,2	
		9.0	20	0-15	45-120	East Site	1.27	0.2	7	7.2	
			49		150-240			0.01		8.1	
		8	25	0-15	45-120	South Site	1.48	0.3	7.5	7.3	
			32		150-240			0.01		7.6	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	>Stolpe, N. B.</author><author>Shea, P. J.</author></authors></contributors><titles><title>Alachlor and Atrazine in a Nebraska Soil and Underlying Sediments</title><secondary-title>Soil Science</secondary-title></titles><periodical><full-title>Soil Science</full-title></periodical><pages>359-370</pages><volume>160</volume><number>5</number><dates><year>1995</year><pub-dates><date>Nov</date></pub-dates></dates><isbn>0038-075X</isbn><accession-num>WOS:A1995TE44600005</accession-										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	num><urls><related-urls><url><style face="underline" font="default" size="100%">&lt;Go to ISI&gt;;//WOS:A1995TE44600005</style></url></related-urls></urls><electronic-resource-num>10.1097/00010694-199511000-00005</electronic-resource-num></record></Cite></EndNote>]										
Aldicarb	Liu et al., 2003 [ADDIN EN.CITE<EndNote><Cite><Author>Liu</Author><Year>2003</Year><RecNum>5324</RecNum><DisplayText><style face="superscript">71</style></DisplayText><record><rec-number>5324</rec-number><foreign-keys><key app="EN" db-	6.1	9.1	0-30	30-80	Not Determined	2.47	1.87	7.93	7.97	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	onic-resource-num></record></Cite></EndNote>]										
Atrazine	Kruger et al., 1997 [ ADDIN EN.CITE <EndNote><Cite><Author>Kruger</Author><Year>1997</Year><RecNum>4401</RecNum><DisplayText><style face="superscript">25</style></DisplayText><record><rec-number>4401</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1522175416" guid="7e5438d2-927a-4c2e-bb41-8bce0aabcd43">4401</key><key app="ENWeb" db-id="">0</key></foreign-keys><ref-type name="Journal Article">17</ref-	50	204	0-30	90-120	fine-loamy, mixed, mesic Aquic hapludoll	2.6	0.6	5.7	6.2	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	type><contributors><authors><author>>Kruger, E. L.</author><author>>Rice, P. J.</author><author>>Anhalt, J. C.</author><author>>Anderson, T. A.</author><author>>Coats, J. R.</author></authors></contributors>><titles><title>Comparative fates of atrazine and deethylatrazine in sterile and nonsterile soils</title><secondary-title>Journal of Environmental Quality</secondary-title></titles><periodical><full-title>Journal of Environmental Quality</full-title></periodical><pages>95-101</pages><volume>26</volume><number>1</number>										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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	Stolpe & Shea, 1995 [ ADDIN EN.CITE <EndNote><Cite><Author>Stolpe</Author><Year>1995</Year><RecNum>4557</RecNum><DisplayText><style face="superscript">21</style></DisplayText><record><rec-number>4557</rec-	13.0	248	0-15	45-120	North Site	1.02	0.33	7.6	7.9	
			113		120-240			0.02		8,2	
		11	107	0-15	45-120	East site	1.27	0.2	7	7.2	
			81		120-240			0.01		8.1	
		27	195	0-15	45-120	South Site	1.48	0.3	7.5	7.3	
			160		120-240			0.01		7.6	

[ PAGE \\* MERGEFORMAT ]



Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradt tw529er" timestamp="1522175453" guid="82290186-eb19-42cc-add2-b8cc1bd068ed">4557</key><key app="ENWeb" db-id="">0</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Stolpe, N. B.</author><author>Shea, P. J.</author></authors></contributors><titles><title>Alachlor and Atrazine in a Nebraska Soil and Underlying Sediments</title><secondary-title>Soil Science</secondary-										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	title></titles><periodical><full-title>Soil Science</full-title></periodical><pages>359-370</pages><volume>160</volume><number>5</number><dates><year>1995</year><pub-dates><date>Nov</date></pub-dates></dates><isbn>0038-075X</isbn><accession-num>WOS:A1995TE44600005</accession-num><urls><related-urls><url><style face="underline" font="default" size="100%">&lt;Go to ISI&gt;;//WOS:A1995TE44600005</style></url></related-urls></urls><electronic-resource-num>10.1097/00010694-199511000-										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	00005</electronic-resource-num></record></Cite></EndNote>]										
	Sarmah <i>et al.</i> , 2009 [ ADDIN EN.CITE <EndNote><Cite><Author>Sarmah</Author><Year>2009</Year><RecNum>5316</RecNum><DisplayText><style face="superscript">62</style></DisplayText><record><record-number>5316</record-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradtw529er" timestamp="1584184603" guid="474a2640-889d-4e9d-9f63-4b9b4957ab16">5316</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author	19	47	0-10	40-50	Waikiwi silt loam 20C	3.9	0.87	5.5	6.7	Graphical <sup>4</sup>
		46	120	0-10	40-50	Waikiwi Silt loam, 7.5 C					
		18	47	0-10	40-50	Motupiko silt loam 20C	2.4	0.26	5.7	6.1	
		34	120	0-10	40-50	Motupiko silt loam, 7.5 C					

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	>Sarmah, Ajit K.</author><author>Close, Murray E.</author><author>Mason, Norman W. H.</author></authors></contributors>><titles><title>Dissipation and sorption of six commonly used pesticides in two contrasting soils of New Zealand</title><secondary-title>Journal of Environmental Science and Health, Part B</secondary-title></titles><periodical><full-title>Journal of Environmental Science and Health, Part B</full-title></periodical><pages>325-336</pages><volume>44</volume><number>4</number>										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	er><dates><year>2009</year><pub-dates><date>2009/05/06</date></p>ub-dates></dates><pu-blisher>Taylor & Francis</publisher><isbn>0360-1234</isbn><urls><related-urls><url>https://doi.org/10.1080/03601230902800960</url></related-urls></uris><electronic-resource-num>10.1080/03601230902800960</electronic-resource-num></record></Cite></EndNote>]										
	Jenks et al. , 1998 [ ADDIN EN.CITE <EndNote><Cite><Author>Jenks</Author><Year>1998</Year><RecNum>4365</RecNum><DisplayText><style face="superscript">24</style></Displ	37.0	60.0	0-30	30-60	Hastings silty clay loam, 20C	1.5	0.6	6.3	6.8	SFO
			22.0		60-90			0.2		7.7	
			87.0		90-120			0.1		7.7	
			193.0		180-210			0.2		7.9	
			223.0		270-300			0.1		7.9	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	and subsurface soil properties on atrazine sorption and degradation</title><secondary-title>Weed Science</secondar y-title></titles><periodical><full-title>Weed Science</full-title></periodical><pages>132-138</pages><volume>46</volume><number>1</number><dates><year>1998</year><pub-dates><date>Jan-Feb</date></pub-dates></dates><isbn>0043-1745</isbn><accession-num>WOS:000072323200022</accession-num><urls><related-urls><url>&lt;Go to ISI&gt;;//WOS:00072323200022</ur										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	l></related-urls></urls></record></Cite></EndNote>]										
	Bedmar et al., 2017 [ ADDIN EN.CITE <EndNote><Cite>< Author>Bedmar</ Author><Year>2017</Year><RecNum>5322</RecNum>< DisplayText><style face="superscript">69</style></DisplayText><record><rec-number>5322</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0wx3e0a0tx0sz3zradttw529er" timestamp="1584184603" guid="4f033275-f25d-4906-ad02-42e15c524367">5322</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors	13.0	16.9 17.9 25.9	0-5	5-41 41-81 81-130	Topsoil General Alvarado Typic Argiudolls, Necochea series	7.48	5.16 2.24 0.43	5.8	5.85 6.65 7.25	
		13.5	14.0 18.4	0-5	5-26 26-51	Topsoil Tres Arroyos Typic Argiudolls, Tres Arroyos series	3.44	2.92 2.06	5.5	5.8 6.05	
			28.6		51-110			0.52	6.45		

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	><authors><author>Bedmar, Francisco</author><author>Gimenez Daniel</author><author>Costa, José Luis</author><author>Daniel, Peter E.</author></authors></contributors><titles><title>Persistence of acetochlor, atrazine, and S-metolachlor in surface and subsurface horizons of 2 typical argudolls under no-tillage</title></titles><pages>3065-3073</pages><volume>36</volume><number>11</number><dates><year>2017</year></dates><isbn>0730-7268</isbn><urls><related-urls><url>https://setac.onlinelibrary.wiley.com/doi/abs										

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	/10.1002/etc.3874 </url></related- urls></urls><electr onic-resource- num>10.1002/etc. 3874</electronic- resource- num></record></C ite></EndNote>]										
	Krutz et al., 2010 [ ADDIN EN.CITE <EndNote><Cite>< Author>Krutz</Aut hor><Year>2010</ Year><RecNum>5080</RecNum><Dis playText><style face="superscript" >72</style></Displ ayText><record><r ec- number>5080</rec -number><foreign- keys><key app="EN" db- id="s0xer2w2o0xw x3e0a0tx0sz3zradt tw529er" timestamp="15221 75676" guid="1016a249- e827-4cc8-b7db- 3876ca9fd8b4">5080</key></foreign-	2	10	0-5	5-15	Colorado, adapted soil	19	19	7.9	8.0	
			25		15-30			19		7.8	
		53	89	0-5	5-15	Colorado, non- adapted soil	15	14	8.1	7.9	
			100		15-30			13		7.9	
		1.0	1.0	0-5	5-15	Mississippi, adapted soil	13	13	6.4	6.3	
			4.5		15-30			13		7.3	
		38	35	0-5	5-15	Mississippi. Non- adapted soil	18	13	6.8	6.6	
			54		15-30			8		6.7	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Krutz, L. J.</author><author>Shaner, D. L.</author><author>Zablotowicz, R. M.</author></authors></contributors><titles><title>Enhanced Degradation and Soil Depth Effects on the Fate of Atrazine and Major Metabolites in Colorado and Mississippi Soils</title><secondary-title>Journal of Environmental Quality</secondary-title></titles><periodical><full-title>Journal of Environmental Quality</full-title></periodical><pages>1369-1377</pages><vol										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	ume>39</volume> <number>4</num ber><dates><year> 2010</year><pub- dates><date>Jul- Aug</date></pub- dates></dates><is bn>0047- 2425</isbn><acces sion- num>WOS:000279 514200027</acces sion- num><urls><relate d-urls><url>&lt;Go to ISI&gt;://WOS:000 279514200027</ur l></related- urls></urls><electr onic-resource- num>10.2134/jeq2 009.0197</electro nic-resource- num></record></C ite></EndNote>]										
Bromacil	Sarmah <i>et al.</i> , 2009 [ ADDIN EN.CITE <EndNote><Cite>< Author>Sarmah</A uthor><Year>2009 </Year><RecNum> 5316</RecNum>< DisplayText><style	12.0	40.0	0-10	40-50	Waikiwi silt loam 20C	3.9	0.87	5.5	6.7	Graphical <sup>4</sup>
		44.0	58.0	0-10	40-50	Motupiko silt loam 20C	2.4	0.26	5.7	6.1	
		92.0	140.0	0-10	40-50	Motupiko silt loam 7.5C					

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	pesticides in two contrasting soils of New Zealand</title><secondary-title>Journal of Environmental Science and Health, Part B</secondary-title></titles><periodical><full-title>Journal of Environmental Science and Health, Part B</full-title></periodical><pages>325-336</pages><volume>44</volume><number>4</number><dates><year>2009</year><pub-dates><date>2009/05/06</date></pub-dates></dates><publisher>Taylor & Francis</publisher><isbn>0360-1234</isbn><urls><related-										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	urls><url>https://doi.org/10.1080/03601230902800960</url></related-urls></urls><electronic-resource-num>10.1080/03601230902800960</electronic-resource-num></record></Cite></EndNote>]										
Chlorotoluron	Gao et al., 2007 [ADDIN EN.CITE<EndNote><Cite><Author>Gao</Author><Year>2007</Year><RecNum>3606</RecNum><DisplayText><style face="superscript">32</style></DisplayText><record><rec-number>3606</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradtw529er" timestamp="1522175197" guid="b73e4391-	147.0	138.6	0-30	30-60	Faster degradation <sup>3</sup>	1.75	0.86	8.09	7.89	SFO
			113.0		60-100		1.75	0.86	8.09	7.89	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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[ PAGE \\* MERGEFORMAT ]



Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	title>International Journal of Environmental Analytical Chemistry</full-title></periodical> <pages>67-76</pages><volume>87</volume><number>1</number><dates><year>2007</year><pubdates><date>Jan 15</date></pubdates></dates><isbn>0306-7319</isbn><accession-num>WOS:000243524400006</accession-num><urls><related-urls><url>&lt;Go to ISI&gt;;//WOS:000243524400006</url></related-urls></urls><electronic-resource-num>10.1080/03067310600847286</electronic-resource-										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	num></record></Cite></EndNote>]										
Chlorthal dimethyl	Di <i>et al.</i> , 1998 [           ADDIN EN.CITE           <EndNote><Cite><           Author>Di</Author>           <Year>1998</Year>           <RecNum>4314</RecNum>           <DisplayText><style           face="superscript">35</style></DisplayText><record><rec-           number>4314</rec-           number><foreign-           keys><key           app="EN" db-           id="s0xer2w2o0xwx3e0a0tx0sz3zradt           tw529er"           timestamp="15221           75394"           guid="2291e218-           5019-4c47-8e66-           45147960a2da">4           314</key><key           app="ENWeb" db-           id="">0</key></for-           eign-keys><ref-           type           name="Journal           Article">17</ref-           type><contributors	40	24	0-25	25-50	Sandy Soil	0.53	0.15	5.3	5.5	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	><authors><author>Di, H. J.</author><author>Aylmore, L. A. G.</author><author>Kookana, R. S.</author></authors></contributors> ><titles><title>Degradation rates of eight pesticides in surface and subsurface soils under laboratory and field conditions</title><secondary-title>Soil Science</secondary-title></titles><periodical><full-title>Soil Science</full-title></periodical><pages>404-411</pages><volume>163</volume><number>5</number><dates><year>1998</year><pub-dates><date>May</date></pub-dates></dates><is										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Flumetsulam	McDowell et al., 1997 [ ADDIN EN.CITE <EndNote><Cite><Author>McDowell </Author><Year>1997</Year><RecNum>5321</RecNum><DisplayText><style face="superscript">68</style></DisplayText><record><rec-	88	70	0-15	15-20	Templeton silt loam 15C	5.73	4.13	5.42	5.51	NR

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	number>5321</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184603" guid="cca49dbfd56c-4b11-af2b-79095c69949a">5321</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>McDowell, R. W.</author><author>Condron, L. M.</author><author>Main, B. E.</author><author>Dastgheib, F.</author></authors></contributors><titles><title>Dissipation of imazapyr, flumetsulam and thifensulfuron in soil</title><secondary-title>Weed										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	Research</second-ary- title></titles><peri- odical><full- title>Weed Research</full- title></periodical> <pages>381- 389</pages><volu- me>37</volume>< number>6</numb- er><dates><year>1 997</year></dates ><isbn>0043- 1737</isbn><urls> <related- urls><url>https://o nlinelibrary.wiley.c om/doi/abs/10.10 46/j.1365- 3180.1997.d01- 73.x</url></relate d- urls></urls><electr- onic-resource- num>10.1046/j.13 65-3180.1997.d01- 73.x</electronic- resource- num></record></C ite></EndNote>]										
Fluometuron		18	21	0-7.5	7.5-15	Beulah silt loam	0.72	0.72	6.8	6.8	SFO

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	Mueller, et al., 1992 [ ADDIN EN.CITE <EndNote><Cite>< Author>Mueller</ Author><Year>199 2</Year><RecNum >4619</RecNum>< DisplayText><style face="superscript" >40</style></Displ ayText><record><r ec- number>4619</rec -number><foreign- keys><key app="EN" db- id="s0xer2w2o0xw x3e0a0tx0sz3zradt tw529er" timestamp="15221 75472" guid="0ca32de2- 7861-4269-ad4f- e67074488b89">4 619</key><key app="ENWeb" db- id="">0</key></for eign-keys><ref- type name="Journal Article">17</ref- type><contributors ><authors><author		31		15-30			0.50		6.9	
			53		30-45			0.38		7.0	
			69		45-60			0.38		7.1	
			144		60-90			0.33		7.2	
			147		90-120			0.31		7.5	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	>Mueller, T. C.</author><author>Moorman, T. B.</author><author>Snipes, C. E.</author></authors></contributors><titles><title>Effect of Concentration, Sorption, and Microbial Biomass on Degradation of the Herbicide Fluometruonf in Surface and Subsurface Soils</title><secondary-title>Journal of Agricultural and Food Chemistry</secondary- title></titles><periodical><full- title>Journal of Agricultural and Food Chemistry</full- title></periodical> <pages>2517- 2522</pages><volume>40</volume> <number>12</nu										

[ PAGE \\* MERGEFORMAT ]



Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Imazapyr	McDowell et al., 1997 [ ADDIN	125.0	155.0	0-15	15-20	Templeton silt loam 15C	5.73	4.13	5.42	5.51	NR

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	EN.CITE <EndNote><Cite><Author>McDowell</Author><Year>1997</Year><RecNum>5321</RecNum><DisplayText><style="superscript">68</style></DisplayText><record><rec-number>5321</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0wx3e0a0tx0sz3zradttw529er" timestamp="1584184603" guid="cca49dbfd56c-4b11-af2b-79095c69949a">5321</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>McDowell, R. W.</author><author>Condron, L. M.</author><auth										

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	or>Main, B. E.</author><author>Dastgheib, F.</author></authors></contributors><titles><title>Dissipation of imazapyr, flumetsulam and thifensulfuron in soil</title><secondary-title>Weed Research</secondary- title></titles><periodical><full- title>Weed Research</full- title></periodical> <pages>381- 389</pages><volume>37</volume><number>6</number><dates><year>1 997</year></dates> <isbn>0043- 1737</isbn><urls> <related- urls><url>https://o nlinelibrary.wiley.c om/doi/abs/10.10 46/j.1365- 3180.1997.d01- 73.x</url></relate										

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	d- urls></urls><electr onic-resource- num>10.1046/j.13 65-3180.1997.d01- 73.x</electronic- resource- num></record></C ite></EndNote>]										
Mecoprop	Helweg, 1993 [ ADDIN EN.CITE <EndNote><Cite>< Author>Helweg</A uthor><Year>1993 </Year><RecNum> 4596</RecNum>< DisplayText><style face="superscript" >43</style></Displ ayText><record><r ec- number>4596</rec -number><foreign- keys><key app="EN" db- id="s0xer2w2o0xw x3e0a0tx0sz3zradt tw529er" timestamp="15221 75467" guid="7f776d09- 4eed-44d5-9bc0- 3ad4c6eb624f">45 96</key><key	7.0	70	0-33	33-66	Jydevad, coarse sandy loam2	N/A	N/A	6.60	6.8	NR
			34		66-99				6.60	6.5	NR

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	241</pages><volume>132</volume><number>2-3</number><dates><year>1993</year><pub- dates><date>Apr 29</date></pub- dates></dates><isbn>0048-9697</isbn><accession- num>WOS:A1993K V41300013</accession- num><urls><related-urls><url><style face="underline" font="default" size="100%">&lt;Go to ISI&gt;;//WOS:A1993KV41300013</style></url></related- urls></urls><electronic-resource- num>10.1016/0048-9697(93)90134- r</electronic- resource- num></record></Cite></EndNote>]										

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	Reffstrup et al., 1998 [ ADDIN EN.CITE <EndNote><Cite>< Author>Reffstrup< /Author><Year>19 98</Year><RecNu m>4322</RecNum ><DisplayText><sty le face="superscript" >44</style></Displ ayText><record><r ec- number>4322</rec -number><foreign- keys><key app="EN" db- id="s0xer2w2o0xw x3e0a0tx0sz3zradt tw529er" timestamp="15221 75397" guid="62900b74- bd0d-44c8-bc03- fba2d61db32a">43 22</key><key app="ENWeb" db- id="">0</key></for eign-keys><ref- type name="Journal Article">17</ref- type><contributors	1.5	8.6	0-15	40-60	0.05 mg/kg load, Flakkebjerg	2.9% humus	0.3% humus	6.10	6.5	NR

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	><authors><author>Reffstrup, T. K.</author><author>Sorensen, H.</author><author>Helweg, A.</author></authors></contributors>><titles><title>Degradation of mecoprop at different concentrations in surface and subsurface soil</title><secondary-title>Pesticide Science</secondary-title></titles><periodical><full-title>Pesticide Science</full-title></periodical><pages>126-132</pages><volume>52</volume><number>2</number><dates><year>1998</year><pubdates><date>Feb</date></pubdates></dates><isbn>0031-										

[ PAGE \\* MERGEFORMAT ]



Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	num></record></Cite></EndNote>]										
Metalaxyl	Di <i>et al.</i> , 1998 [ ADDIN EN.CITE <EndNote><Cite>< Author>Di</Author ><Year>1998</Yea r><RecNum>4314< /RecNum><Display Text><style face="superscript" >35</style></Displ ayText><record><r ec-number>4314</rec -number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradt tw529er" timestamp="15221 75394" guid="2291e218-5019-4c47-8e66-45147960a2da">4 314</key><key app="ENWeb" db-id="">0</key></for eign-keys><ref-type name="Journal Article">17</ref-type><contributors	48	117	0-25	25-50	Sandy Soil	0.53	0.15	5.3	5.5	SFO

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	><authors><author>Di, H. J.</author><author>Aylmore, L. A. G.</author><author>Kookana, R. S.</author></authors></contributors>><titles><title>Degradation rates of eight pesticides in surface and subsurface soils under laboratory and field conditions</title><secondary-title>Soil Science</secondary-title></titles><periodical><full-title>Soil Science</full-title></periodical><pages>404-411</pages><volume>163</volume><number>5</number><dates><year>1998</year><pub-dates><date>May</date></pub-dates></dates><is										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Metolachlor	Rice et al., 2002 [ADDIN EN.CITE<EndNote><Cite><Author>Rice</Author><Year>2002</Year><RecNum>4002</RecNum><DisplayText><style face="superscript">45</style></DisplayText><record><rec-number>4002</rec-number></foreign-	81	289	0-30	90-120	Nicollet, fine-loamy, mixed, mesic Typic Haplquoll	1.5	0.2	5.5	7.9	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	elibrary.wiley.com/store/10.1002/etc.5620211216/asset/5620211216_ftp.pdf?v=1&amp;t=j1n nlz82&amp;s=9e0b1963bbc668a49d0994c1e2a14a91932ce2fe</url></related-urls></urls><electronic-resource-num>10.1897/1551-5028(2002)021<2640:dapomi>2.0.co;2</electronic-resource-num></record></Cite></EndNote>]										
	Si, et al., 2009 [ADDIN EN.CITE<EndNote><Cite><Author>Si</Author><Year>2009</Year><RecNum>3269</RecNum><DisplayText><style face="superscript">46</style></DisplayText><record><rec-number>3269</rec-number></foreign-	5.0	11.7	0-50	50-100	Tsukuba clay loam	N/A	N/A	6.30	6.34	
			23.8		100-200						
			53.3		200-300						
			68.6		300-350						
			133.3		350-425						
			72.2		425-500						

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	l><url>http://onlin elibrary.wiley.com/ store/10.1002/ps.1 779/asset/1779_ft p.pdf?v=1&amp;t=j 1nnnfp8&amp;s=2 0cc85023ff7ba153 3e1ed4c2284aba2 335b5d19</url></r elated- urls></urls><electr onic-resource- num>10.1002/ps.1 779</electronic- resource- num></record></C ite></EndNote>]										
Oxadixyl	Mosquera-Vivas, et al., 2016 [ ADDIN EN.CITE <EndNote><Cite>< Author>Mosquera- Vivas</Author><Ye ar>2016</Year><R ecNum>5325</Rec Num><DisplayText ><style face="superscript" >73</style></Displ ayText><record><r ec- number>5325</rec -number><foreign- keys><key	57.8	57.8	0-20	20-40	10.3	4.8	6.3	5.3		
			53.3		40-60						
			86.6		60-80		2.7		5.4		
			990.2		80-100						

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	of carbofuran and oxadicyl in a Colombian agricultural soil profile %J Agronomía Colombiana</title></titles><pages>92-100</pages><volume>34</volume><dates><year>2016</year></dates><isbn>0120-9965</isbn><urls><related-urls><url>http://www.scielo.org.co/scielo.php?script=sci_arttext&pid=S0120-99652016000100011&nrm=iso</url></related-urls></urls></record></Cite></EndNote>]										
Procymidone	Sarmah <i>et al.</i> , 2009 [ ADDIN EN.CITE <EndNote><Cite><Author>Sarmah</Author><Year>2009</Year><RecNum>	9	24	0-10	40-50	Waikiwi silt loam 20C	3.9	0.87	5.5	6.7	Graphical <sup>4</sup>
		10	120	0-10	40-50	Waikiwi silt loam 7.5C					
		37	48	0-10	40-50	Motupiko silt loam, 20 C	2.4	0.26	5.7	6.1	

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	sorption of six commonly used pesticides in two contrasting soils of New Zealand</title><secondary-title>Journal of Environmental Science and Health, Part B</secondary-title></titles><periodical><full-title>Journal of Environmental Science and Health, Part B</full-title></periodical><pages>325-336</pages><volume>44</volume><number>4</number><dates><year>2009</year><pub-dates><date>2009/05/06</date></pub-dates></dates><publisher>Taylor & Francis</publisher><isbn>0360-										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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Prometryne	Di et al., 1998 [ADDIN EN.CITE<EndNote><Cite><Author>Di</Author><Year>1998</Year><RecNum>4314</RecNum><DisplayText><style face="superscript">35</style></DisplayText><record><rec-number>4314</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0wx3e0a0tx0sz3zradttw529er" timestamp="15221	64	141	0-25	25-50	Sandy soil	0.53	0.15	5.3	5.5	SFO
Propyzamide		92	64	0-25	25-50	Sandy soil	0.53	0.15	5.3	5.5	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	<p>75394"</p> <p>guid="2291e218-5019-4c47-8e66-45147960a2da"&gt;4314&lt;/key&gt;&lt;key app="ENWeb" db-id=""&gt;0&lt;/key&gt;&lt;/foreign-keys&gt;&lt;ref-type name="Journal Article"&gt;17&lt;/ref-type&gt;&lt;contributors&gt;&lt;authors&gt;&lt;author&gt;Di, H. J.&lt;/author&gt;&lt;author&gt;Aylmore, L. A. G.&lt;/author&gt;&lt;author&gt;Kookana, R. S.&lt;/author&gt;&lt;/authors&gt;&lt;/contributors&gt;&lt;titles&gt;&lt;title&gt;Degradation rates of eight pesticides in surface and subsurface soils under laboratory and field conditions&lt;/title&gt;&lt;secondary-title&gt;Soil Science&lt;/secondary-title&gt;&lt;/titles&gt;&lt;/periodical&gt;&lt;full-</p>										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
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s-Metolachlor	Bedmar et al., 2017[ ADDIN	81.5	110.0	0-5	5-41	Topsoil General Alvarado Typic	7.48	5.16	5.8	5.85	
			113.6		41-81		7.48	2.24	5.8	6.65	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	EN.CITE <EndNote><Cite><Author>Bedmar</Author><Year>2017</Year><RecNum>5322</RecNum><DisplayText><style face="superscript">69</style></DisplayText><record><record-number>5322</record-number><foreign-keys><key app="EN" db-id="s0xer2w2o0wx3e0a0tx0sz3zradttw529er" timestamp="1584184603" guid="4f033275-f25d-4906-ad02-42e15c524367">5322</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Bedmar, Francisco</author><author>Gimenez, Daniel</author><a		126.0		81-130	Argjudolls, Necochea series	7.48	0.43	5.8	7.25	
		82.5	94.9	0-5	5-26	Topsoil Tres Arroyos Typic Argjudolls, Tres Arroyos series	3.44	2.92	5.5	5.8	
			133.3		26-51		3.44	2.06	5.5	6.05	
			141.4		51-110		3.44	0.52	5.5	6.45	

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	uthor>Costa, José Luis</author><author>Daniel, Peter E.</author></authors></contributors><titles><title>Persistence of acetochlor, atrazine, and S-metolachlor in surface and subsurface horizons of 2 typic argiudolls under no-tillage</title></titles><pages>3065-3073</pages><volume>36</volume><number>11</number><dates><year>2017</year></dates><isbn>0730-7268</isbn><urls><related-urls><url>https://setac.onlinelibrary.wiley.com/doi/abs/10.1002/etc.3874</url></related-urls></urls><electronic-resource-num>10.1002/etc.3874</electronic-										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	resource-num></record></Cite></EndNote>]										
Terbuthylazine	Sarmah <i>et al.</i> , 2009 [ ADDIN EN.CITE <EndNote><Cite><Author>Sarmah</Author><Year>2009</Year><RecNum>5316</RecNum><DisplayText><style face="superscript">62</style></DisplayText><record><rec-number>5316</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184603" guid="474a2640-889d-4e9d-9f63-4b9b4957ab16">5316</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Sarmah, Ajit	10.0	24.0	0-10	40-50	Waikiwi silt loam 20C	3.9	0.87	5.5	6.7	Graphical <sup>4</sup>
	16.0	36.0	0-10	40-50	Waikiwi silt loam 7.5C						
	24.0	31.0	0-10	40-50	Motupiko silt loam 20C	2.4	0.26	5.7	6.1		
	42.0	80.0	0-10	40-50	Motupiko silt loam 7.5C						

[ PAGE \\* MERGEFORMAT ]

Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	K. Close, Murray E. Mason, Norman W. H. </author></authors></contributors><titles><title>Dissipation and sorption of six commonly used pesticides in two contrasting soils of New Zealand</title><secondary-title>Journal of Environmental Science and Health, Part B</secondary-title></titles><periodical><full-title>Journal of Environmental Science and Health, Part B</full-title></periodical><pages>325-336</pages><volume>44</volume><number>4</number><dates><year>2										

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Pesticide	Source	DT50, T <sub>1/2</sub> (days)		Depth (cm)		Soil or Comment	% OC or NOM		pH		Kinetic Equation
		Surface	Subsurface	Surface	Subsurface		Surface	Subsurface	Surface	Subsurface	
	009</year><pub- dates><date>2009 /05/06</date></p ub- dates></dates><pu blisher>Taylor & Francis</publisher ><isbn>0360- 1234</isbn><urls> <related- urls><url>https://d oi.org/10.1080/03 601230902800960 </url></related- urls></urls><electr onic-resource- num>10.1080/036 01230902800960< /electronic- resource- num></record></C ite></EndNote>]										

NR=not reported; OC=organic carbon; NOM=natural organic matter; DT50=time to 50% loss; FOMC= Gustafson and Holden Model; SFO=single-first order;

DFOP=double first order in parallel

1 Fine montmorillonitic, mesic Cumilic Haplaquoll)

2 Estimated value (4 replicates); 0.05mg/kg mecoprop; 10C, water at 50% WHC

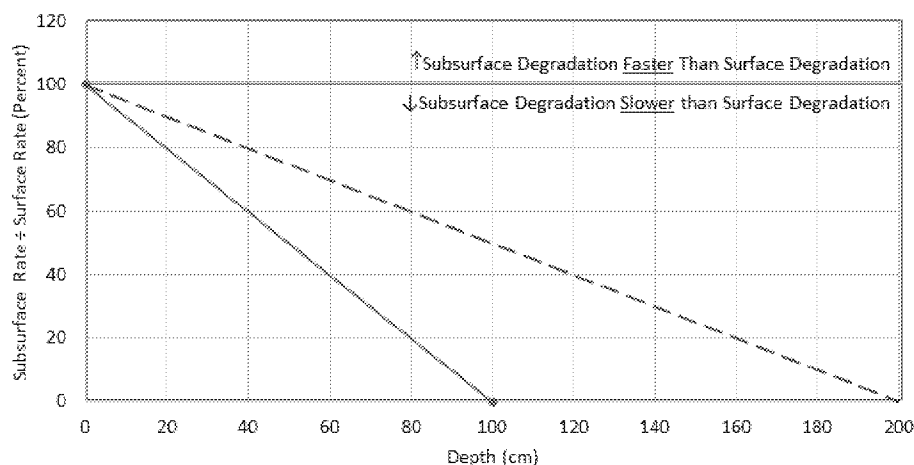
3 Faster degradation attributed to lower OM and sorption at lower depths increasing bioavailability

4 Not described well with SFO

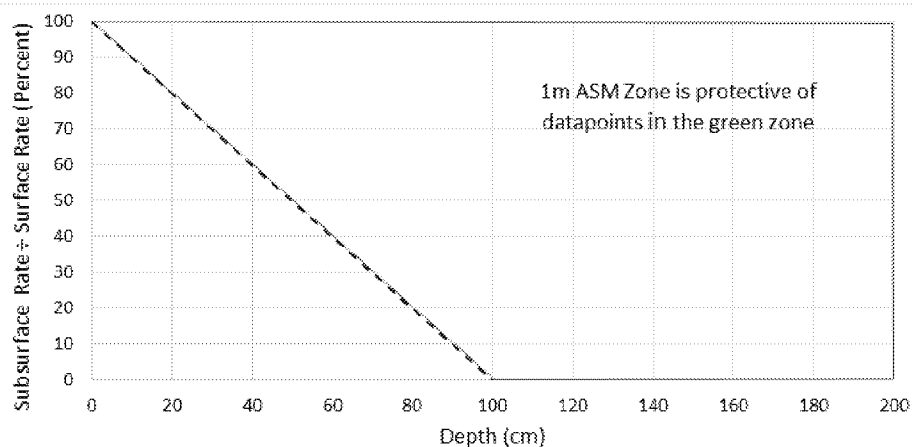
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# Appendix [SEQ Appendix \\* ALPHABETIC]. Relative Rates of Surface and Subsurface Metabolism Rates by Depth (Summary of Open Literature Data)

In order to understand how measured data compared with the current standard conceptual model for modeling open literature data were graphed along with the conceptual model. The standard conceptual model assumes that the rate of subsurface degradation is a fraction of the surface ASM rate and that fraction declines linearly from 1 to zero at 1 meter. In the graph, the x-axis was the midpoint of the soil layer collected for the experiment. Surface layer results were graphed at zero depth. The y-axis was graphed as the subsurface rate of degradation divided by the surface rate of degradation times 100. When the y-axis values are greater than 100, subsurface degradation was faster than surface degradation, which occurred for some datasets. This is illustrated by the orange shading in **Figure B1(a)**. When the y-axis is below 100, subsurface degradation was slower than surface degradation, shaded in green in figure B1(a). Dashed lines for the standard conceptual model where ASM declines to zero at 1-meter (dashed gray line;  $y = -1x + 100$ ) and for the potential assumption of declining to zero at 2-meters (dashed purple line;  $y = -0.5x + 100$ ) were included in the figures. Figure B1(b) shows areas of the Figure where data occur where the dashed lines would or would not be considered protective of the measured data.



(a) Explanation of when subsurface degradation is faster or slower than surface degradation rates.



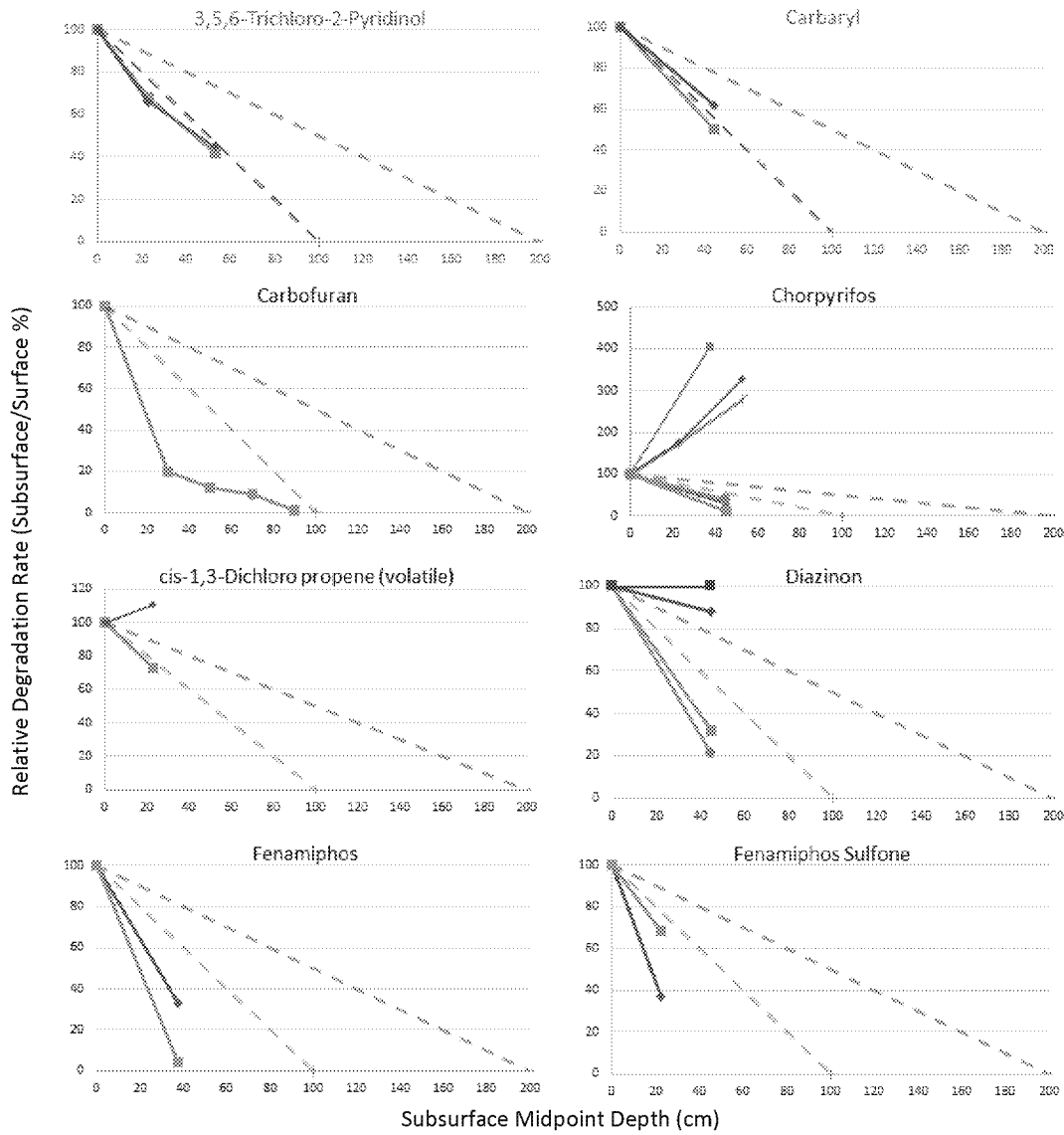
(b) The 1m ASM Zone Assumption Predicts Slower Subsurface Degradation for Datapoints in the Green Zone

Figure B1. Graph Interpretation Explanation for the Subsurface to Surface Degradation Rate Ratio Graph

Open literature results were included in the following graphs when measured data were available for a surface and subsurface soil at the same location and the subsurface rate was slower. Data were split into data where the chemical may undergo hydrolysis and data where the chemical was stable to abiotic hydrolysis, so that any degradation observed could be assumed to be biotically mediated for this dataset.

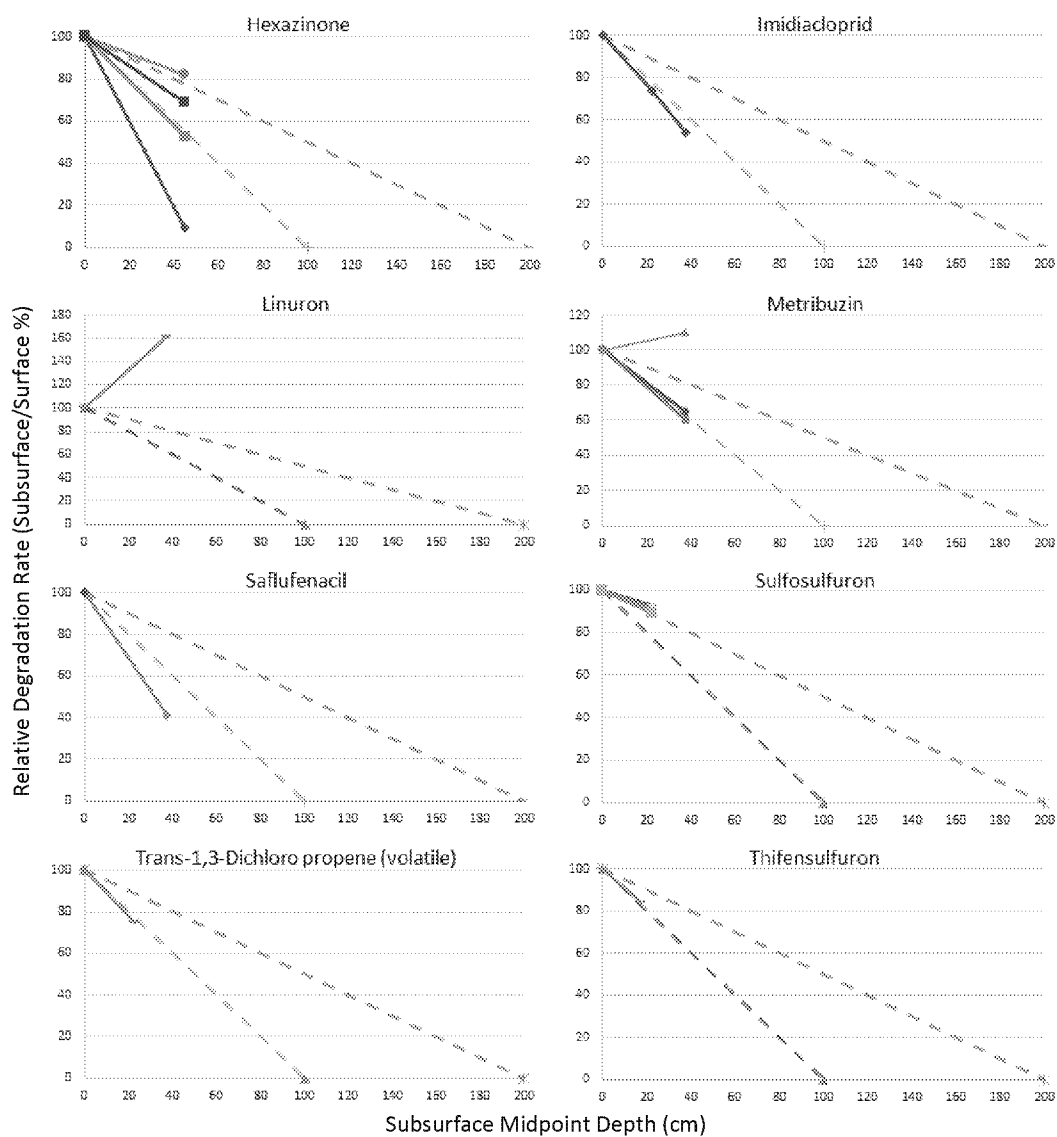


Open Literature Subsurface Data Compared to 1-meter and 2-meter Zones of Degradation for  
Chemicals that Undergo Hydrolysis



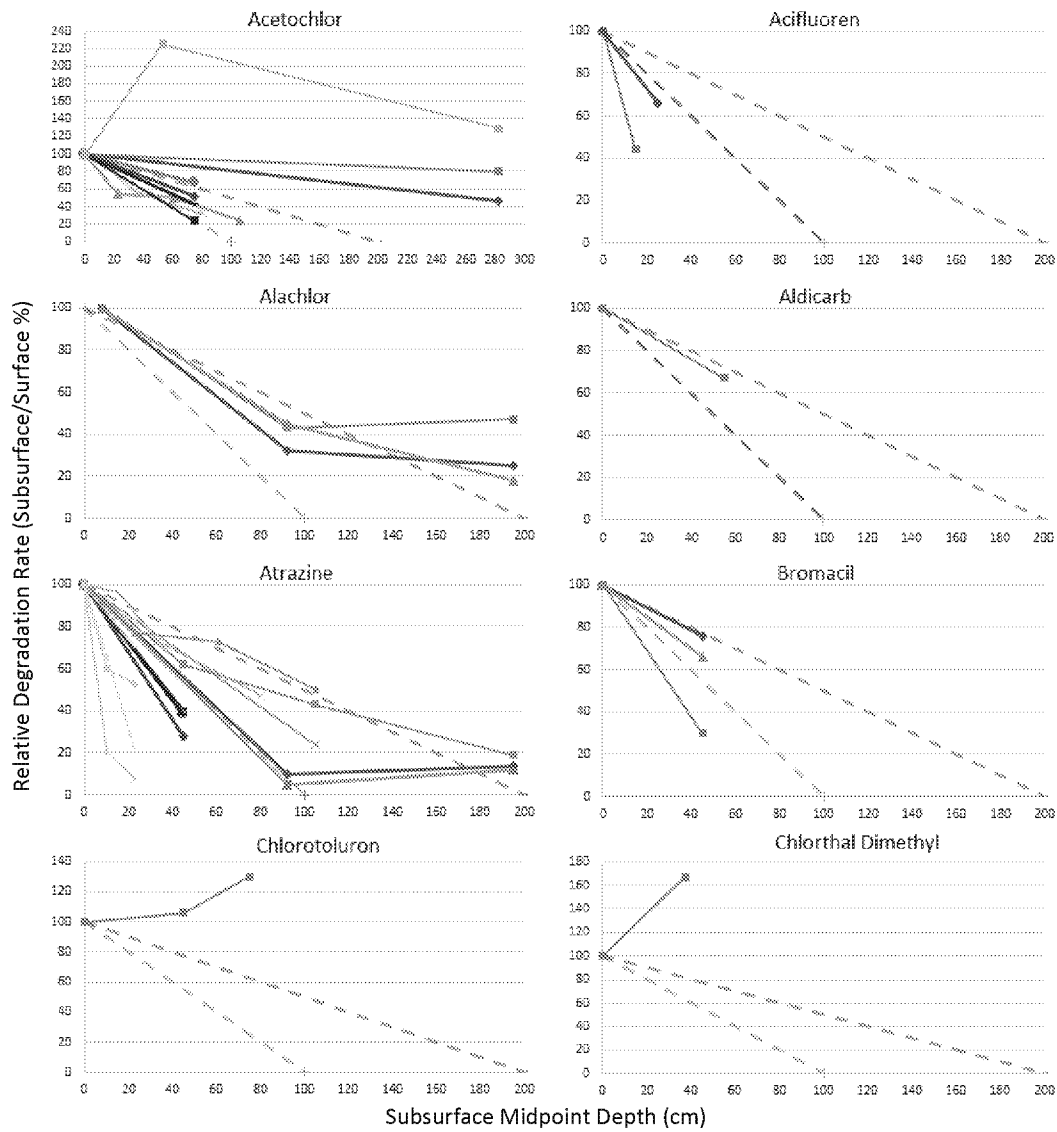
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Open Literature Subsurface Data Compared to 1-meter and 2-meter Zones of Degradation for  
Chemicals that Undergo Hydrolysis



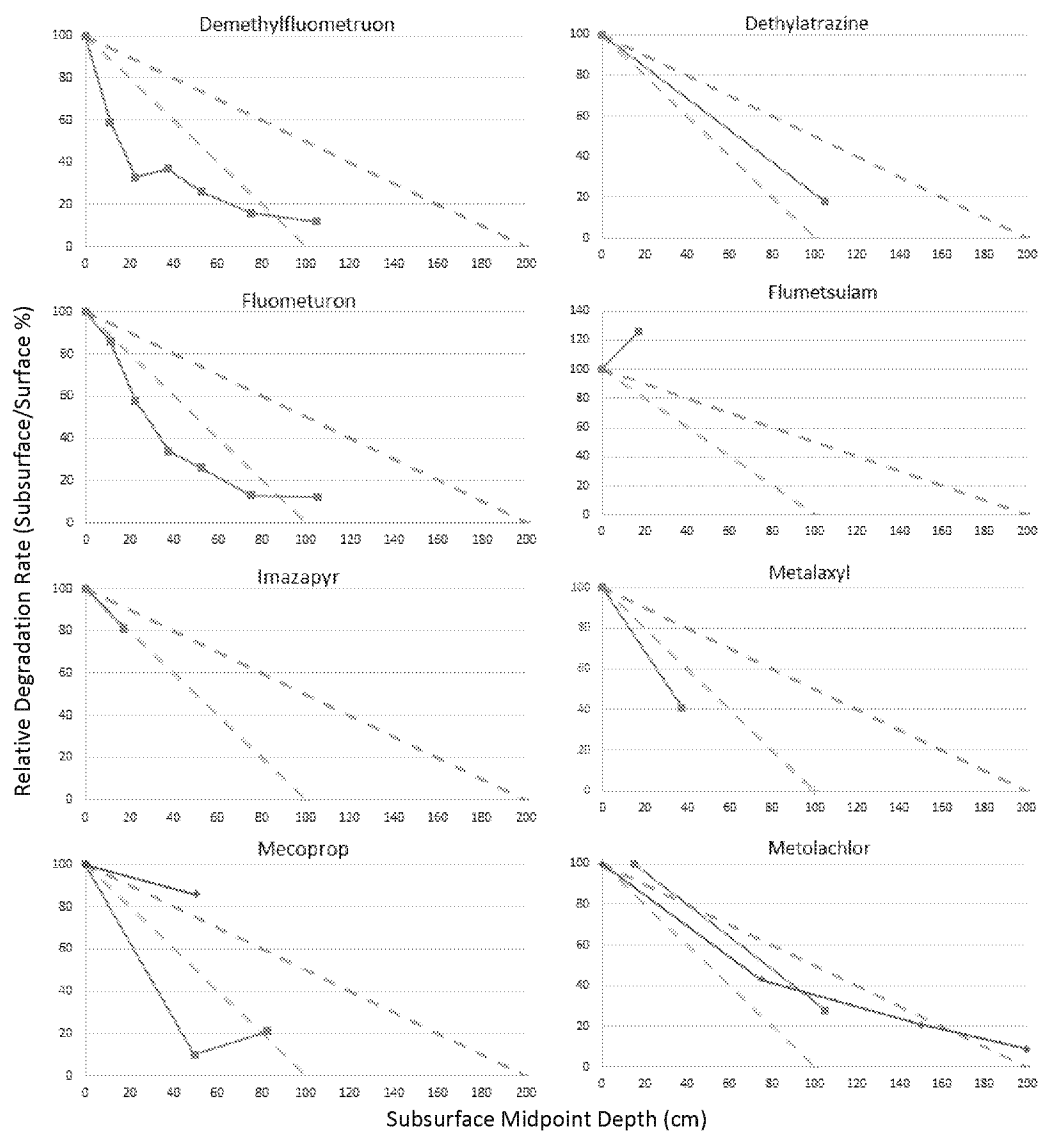
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Open Literature Subsurface Data Compared to 1-meter and 2-meter Zones of Degradation for  
Chemicals that Stable to Hydrolysis



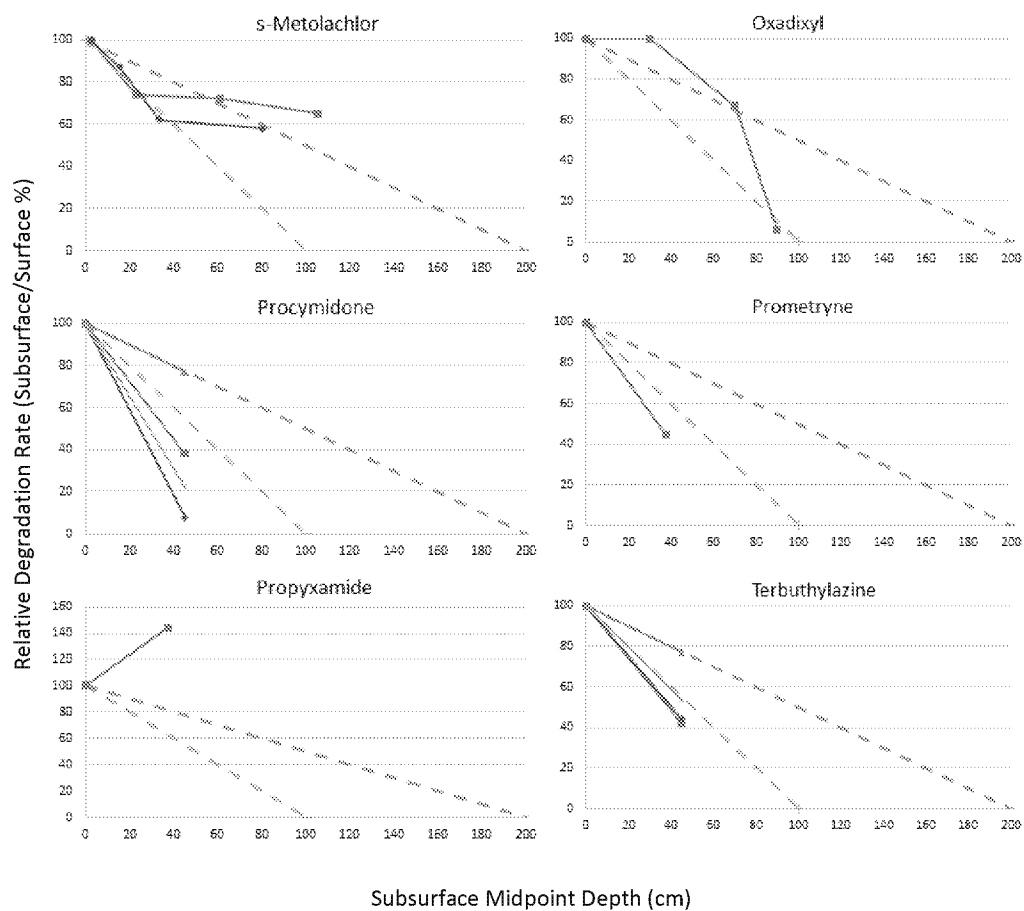
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Open Literature Subsurface Data Compared to 1-meter and 2-meter Zones of Degradation for  
Chemicals that Stable to Hydrolysis



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Open Literature Subsurface Data Compared to 1-meter and 2-meter Zones of Degradation for  
Chemicals that Stable to Hydrolysis



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## Appendix [SEQ Appendix \\* ALPHABETIC]. Comparison Aerobic Soil Metabolism Results from Open Literature and Registrant Submitted Studies

Aerobic soil (surface soil) half-life data submitted to EFED by registrants was compared with surface (aerobic) soil half-life data from the open literature to determine if half-life values for the same pesticide from the two datasets were similar. R statistical software version. 3.5.3 [ ADDIN EN.CITE <EndNote><Cite><Author>R Core

Team</Author><Year>2019</Year><RecNum>5326</RecNum><DisplayText><style face="superscript">74</style></DisplayText><record><rec-number>5326</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184604" guid="faa7775e-ec58-4fd4-9a91-be58dc540e0e">5326</key></foreign-keys><ref-type name="Computer Program">9</ref-type><contributors><authors><author>R Core Team,</author></authors></contributors><titles><title>R: A language and environment for statistical computing</title></titles><dates><year>2019</year></dates><pub-location>Vienna, Austria</pub-location><publisher>R Foundation for Statistical Computing</publisher><urls><related-urls><url>https://www.R-project.org</url></related-urls></urls></record></Cite></EndNote>] was used for all analyses, with the 'psych' [ ADDIN EN.CITE <EndNote><Cite

ExcludeYear="1"><Author>Revelle</Author><Year>2018</Year><RecNum>5327</RecNum><DisplayText><style face="superscript">75</style></DisplayText><record><rec-number>5327</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184604" guid="5a8a0b24-f8f3-479c-b659-9c039824323d">5327</key></foreign-keys><ref-type name="Computer Program">9</ref-type><contributors><authors><author>Revelle, W.</author></authors></contributors><titles><title>psych: Procedures for Personality and Psychological Research</title></titles><dates><year>2018</year></dates><pub-location>Evanston, IL</pub-location><publisher>Northwestern University</publisher><urls><related-urls><url>https://cran.r-project.org/web/packages/psych/index.html</url></related-urls></urls></record></Cite></EndNote>] being used for all summary statistics, and the 'ggplot2' package [ ADDIN EN.CITE <EndNote><Cite

ExcludeYear="1"><Author>Wickham</Author><Year>2016</Year><RecNum>5328</RecNum><DisplayText><style face="superscript">76</style></DisplayText><record><rec-number>5328</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184604" guid="1ecfd8f6-e5ca-4a2b-97d5-a3ac6074cb27">5328</key></foreign-keys><ref-type name="Computer Program">9</ref-type><contributors><authors><author>Wickham, H</author></authors></contributors><titles><title>ggplot2: Elegant Graphics for Data

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Analysis</title></titles><dates><year>2016</year></dates><pub-location>New York, NY</pub-location><publisher>Springer-Verlag</publisher><urls><related-urls><url>https://ggplot2.tidyverse.org</url></related-urls></urls></record></Cite></EndNote>] used for all figures. Data are summarized in **Table C1**.

Analysis of variance (ANOVA) was conducted separately for each of the pesticides, and if this analysis suggested that mean half-life values differed ( $p < 0.05$ ) between the registrant-submitted and open literature datasets, two-sided mean comparisons tests were used to determine the nature of the difference (see **Table C1**). Assumptions of normality and homoscedasticity for the datasets were tested prior to mean comparison tests using Shapiro-Wilk's and Bartlett's tests, respectively, with  $\alpha = 0.01$  per EFED standard statistical practices.

Of the 10 pesticides more than two datapoints available in both datasets, the only pesticide for which the initial ANOVA determined that mean half-lives were significantly ( $p < 0.05$ ) different was alachlor ( $p$ -value = 0.008 (see **Figure C1**). The alachlor soil half-life data met both assumptions for parametric testing and therefore the means in the two registrant and open literature datasets were further compared using a Student's  $t$  test. This post hoc mean comparison test confirmed that the mean aerobic soil-life from the open literature was significantly ( $p < 0.05$ ) lower than that from the available registrant data. The open literature alachlor dataset has three measured half-life values (8, 9, and 9) for soils that were all collected from adjacent fields near Shelton, Nebraska. The sites and soils don't have the variability in the soils that we see across registrant submitted studies. This could explain why there was a difference in the open literature values in comparison to the registrant submitted study results.

**Table C1. Comparison of Registrant Submitted and Open Literature Aerobic Soil Metabolism Data**

Pesticide	EFED				Open Literature				ANOVA p-value
	N	Mean	Min	Max	N	Mean	Min	Max	
Acetochlor	2	11	8	14	9	14	6.5	24	0.52
Acifluorfen	4	150	100	200	2	91	74	108	0.23
Alachlor	3	30	26	34	3	8.7	8.0	9.0	<0.008
Aldicarb	7	8	1	17	1	6.1	6.1	6.1	0.71
Atrazine	1	146	146	146	15	25	1.0	53	--
Carbaryl	4	39	3.8	95.1	2	8.5	8.0	9.0	0.37
Carbofuran	1	321	321	321	1	11	11	11	--
Chlorotoluron	1	59	59	59	1	148	148	148	--
Chlorpyrifos	8	119	19	297	6	55	11	154	0.19
Chlorthal dimethyl	7	33	16.6	48	1	40	40	40	--
cis-1,3-Dichloropropene	2	33	12	54	2	14	8.0	20	0.47
Diazinon	5	20	4.36	56.6	4	8.0	5.0	12	0.32
Flumetsulam	2	72	13	130	1	88	88	88	--

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Pesticide	EFED				Open Literature				ANOVA p-value
	N	Mean	Min	Max	N	Mean	Min	Max	
Fluometuron	1	181	181	181	1	18	18	18	--
Imazapyr	1	365	365	365	1	125	125	125	--
Linuron	5	199	57.6	365	1	142	142	142	--
Mecoprop	4	19	14.8	30.1	2	4.3	1.5	7.0	0.06
Metalaxyl	5	44	10.1	85.8	1	48	48	48	--
Metolachlor	4	37	13.9	67	2	43	5.0	81	0.84
Metribuzin	1	74	73.7	73.7	4	109	32	212	--
Oxadixyl	1	180	180	180	1	58	58	58	--
Prometryne	6	112	15	279	1	64	64	64	--
Propyzamide	3	29	20.1	44.6	1	92	92	92	--
trans-1,3-Dichloropropene	2	33	12	54	1	17	17	17	--

N=number of measured values in the dataset

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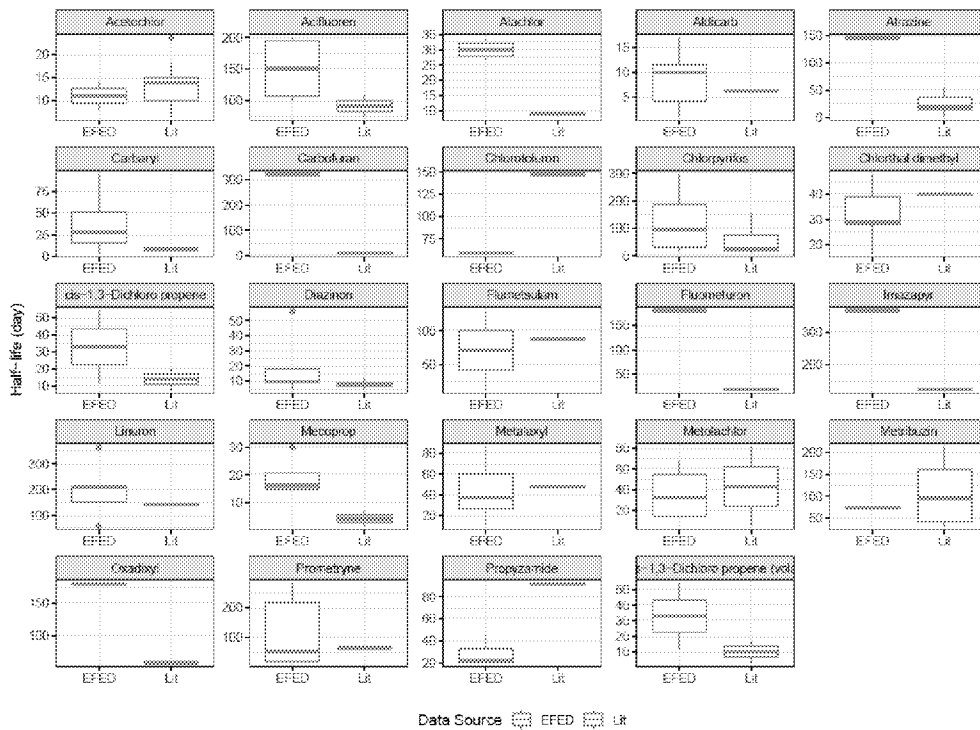


Figure C1. Comparison of Surface Aerobic Soil Metabolism Half-life Values for Pesticides with Data Available from Registration Submitted Studies (EFED) and in the Open Literature (Lit)

## Appendix [ SEQ Appendix \\* ALPHABETIC ], Impact of Changing Modeling Assumptions on EDWCs

In this appendix, the impact of changing the PWC model to allow ASM to be extended to deeper depths is investigated in **Section D1**. Two different changes to model assumptions are evaluated. The first modification incrementally extends the depth to which ASM occurs and is discussed in **Section D2**. The second modification assumes changing the model inputs by assuming a background degradation rate (**Section D3**). Finally, combinations of both changes are also evaluated. **Section D4** examines the change in EDWCs for the pesticides used to compare to PGW and WQP monitoring in subsequent sections.

The following model assumption abbreviations are used throughout this document:

- 1m0x – current modeling assumptions of ASM declining to zero at 1 m depth and no change to the abiotic hydrolysis input
- 2m0x, 3m0x, and 4m0x – ASM declining to zero at 2, 3, and 4 meters, respectively, from the surface and no change to the abiotic hydrolysis input
- 1m10x and 1m25x – ASM declining to zero at 1 m from the surface and the hydrolysis half-life was assumed to be 10x or 25x, respectively, the ASM half-life. Examined only for chemicals that do not undergo hydrolysis
- 2m10x, 2m25x, 3m10x, 3m25x, 4m10x and 4m25x – defined similarly as above.

### D1. Current PWC Groundwater Degradation Pathways (Response Analysis)

There are two degradation pathways (abiotic hydrolysis and ASM) considered in PWC GW modeling. To assess the impact that these two transformation pathways on EDWCs, abiotic hydrolysis and ASM inputs were varied and the resulting EDWCs plotted. The impact of both pathways are depicted in the four graphs of **Figure D1**, which show peak (left-side graphs) and post-breakthrough average (right-side graphs) EDWCs as a function of Koc and either abiotic hydrolysis (**Figures D1a and b**) or ASM (**Figures D1c and d**) half-life. In these graphs, the other degradation pathway is stable (*i.e.*, ASM is stable in the hydrolysis graphs, and *vice versa*). All other model inputs are the same. Applications were assumed to occur on the first of every month for 12 months and the pesticide was non-volatile. The EDWCs depicted at each point in the graphs is the highest EDWC predicted by any of the six standard GW scenarios. Abiotic hydrolysis is modeled by PWC GW as constant throughout the soil profile but is assumed to only occur in the dissolved phase, while ASM only occurs in the top 1 meter of the soil profile (declining with depth), but in both the dissolved and sorbed phases.

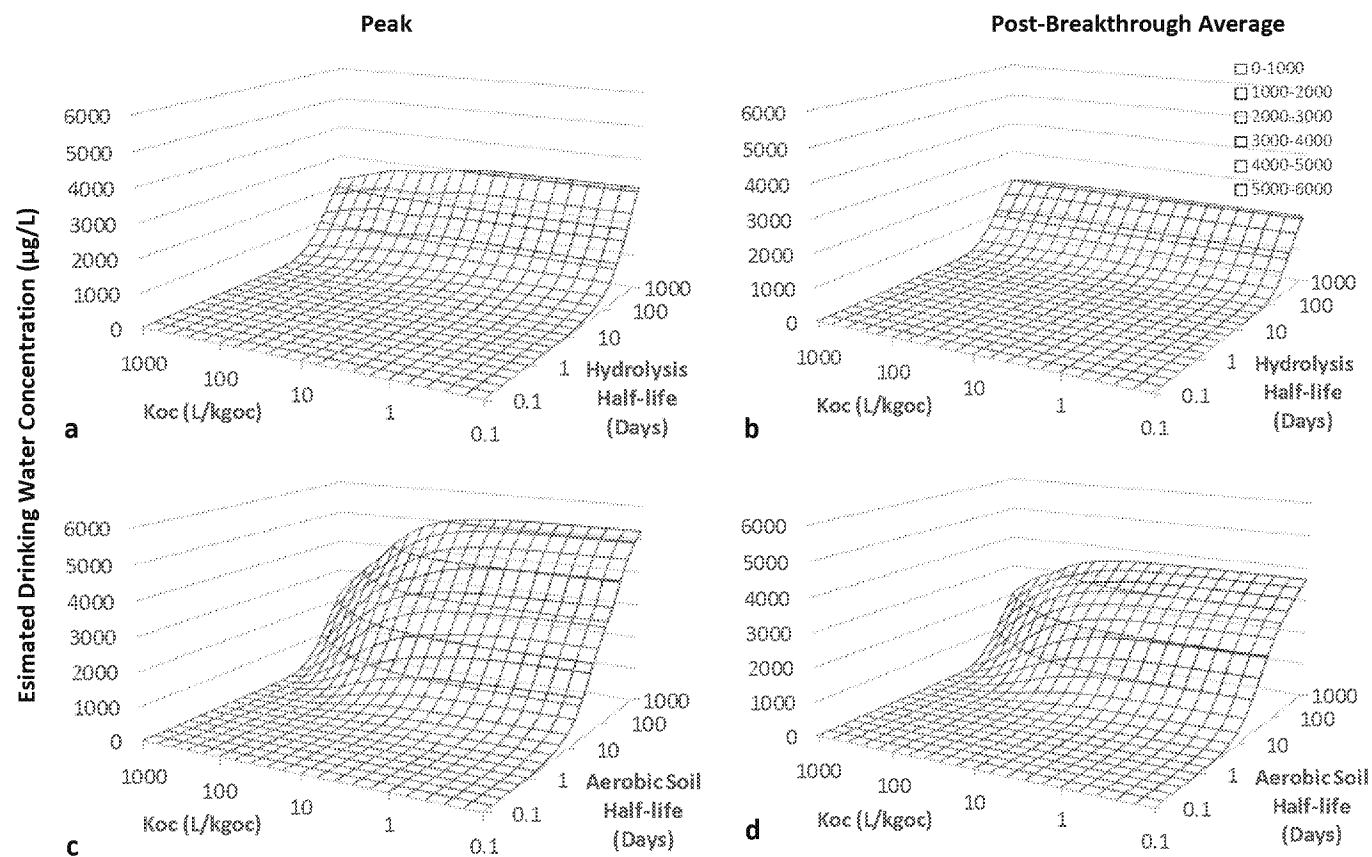


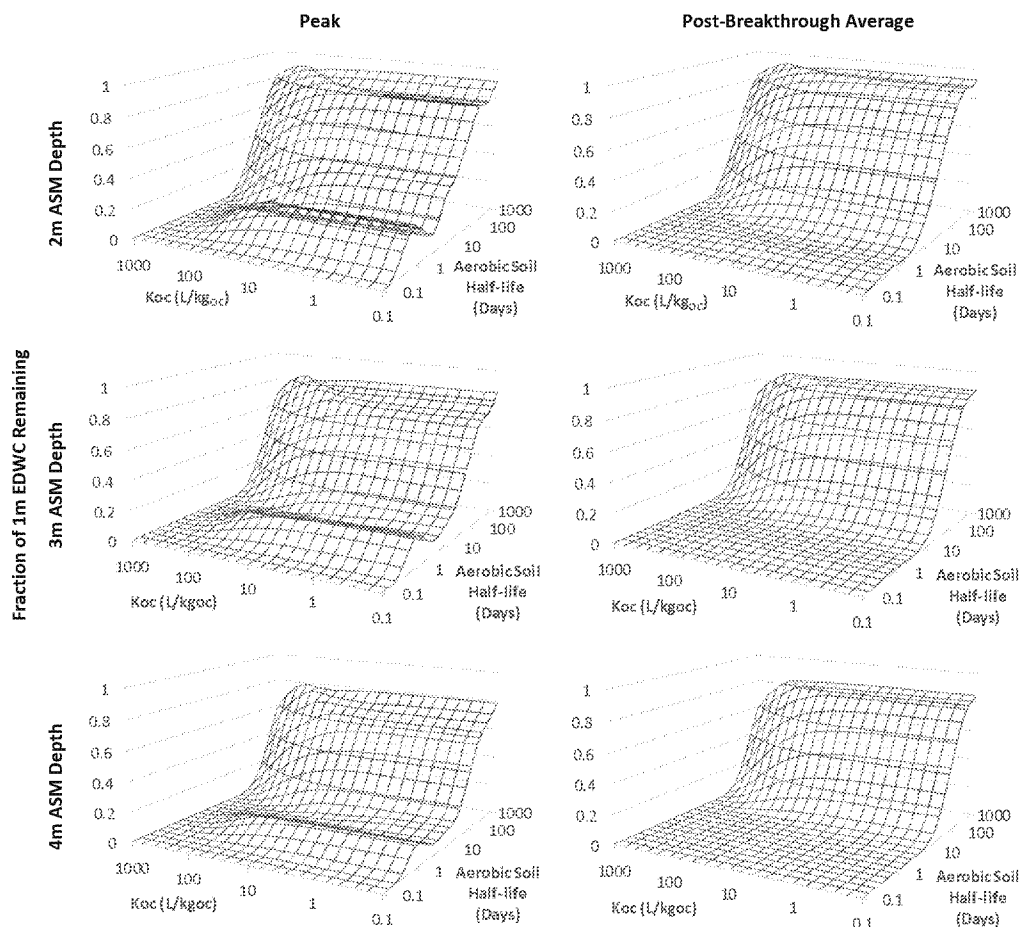
Figure D1. Demonstration of the Impact of Abiotic Hydrolysis (a and b, ASM stable) and Aerobic Soil Metabolism (c and d; Hydrolysis Stable) on Peak (a and c) and Post-breakthrough Average (b and d) Groundwater Drinking Water Concentrations

For any given scenario, all chemicals move at similar velocities with the downward movement of water in the dissolved phase. Therefore, all chemicals will spend similar amounts of time subject to dissolved phase degradation. Since hydrolysis only occurs in the dissolved phase, K<sub>oc</sub> largely does not impact EDWCs affected solely by abiotic hydrolysis degradation alone. This is illustrated in the **Figure D1 a and b** with no change in the EDWCs across K<sub>oc</sub> values evaluated.

However, K<sub>oc</sub> controls the amount of time that a chemical spends in the sorbed phase with higher K<sub>oc</sub> values leading to more time for sorbed phase ASM degradation. Because ASM is modeled as occurring in both the dissolved and sorbed phases, ASM is greatly enhanced (reduced EDWCs) at higher K<sub>oc</sub> values (**Figure D1c and d**). Notice also that for low K<sub>oc</sub> values, an abiotic hydrolysis half-life alone (no ASM) will produce a greater reduction in EDWC than the numerically similar ASM half-life alone (no hydrolysis) due to hydrolysis occurring throughout the entire soil profile and not declining with depth as ASM degradation is modeled. Conversely, at high K<sub>oc</sub> values (somewhere >1000 L/kg-oc), an ASM half-life produces a greater reduction in EDWC than a numerically similar abiotic hydrolysis half-life (related to the long residence time of the chemical in the upper soil layers where the ASM rate is greatest).

#### Section D2. Impact of ASM Degradation Zone Depth on EDWCs

This section describes how predicted concentrations for pesticides in a range of mobility and persistence classes change with different assumptions on the depth of the ASM zone of degradation. To do this, the fraction of the current standard 1 m ASM depth EDWC remaining after the ASM depth is incrementally increased to 2, 3, and 4 meters is depicted in **Figure D2** on the y-axis for different K<sub>oc</sub> on the x-axis and ASM on the z-axis. These graphs are like those used to depict the impact of ASM in **Figure D1**, with the exception that the y-axis has been changed from EDWC in concentration units in **Figure D1** to a unitless fraction of the 1-meter ASM depth EDWC remaining with different ASM depths in **Figure D2**.



**Figure D2. Impact of changing Aerobic Soil Metabolism (ASM) Depth on EDWCs (fraction of standard 1m ASM Depth EDWC remaining) across Koc and ASM Half-life.**

Expressed as in **Figure D2**, the continuous variation of the fraction remaining in each graph can be readily described in terms of different “regions” (defined in terms of ASM half-life and Koc) where the change in ASM depth produces:

- a large change from the 1-meter EDWCs (anywhere in these graphs where the fraction remaining is near zero, for example pesticides with an ASM of 100-days and lower);
- a limited change (anywhere that the fraction remaining is near one, for example pesticides with an ASM of 1000-days), and
- a zone transition between the large and limited impact zones (for example pesticides with ASM between 100 and 1000-days).

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**Figure D3** shows the same information as that displayed in **Figure D2**, but in a bar graph. Lastly, it should be noted that chemicals that undergo abiotic hydrolysis and are stable to ASM would be insensitive to changes in ASM depth.

The limited change zone indicates the combinations of Koc (higher mobility, lower Koc) and ASM (larger half-lives) where PWC is relatively insensitive to changing ASM depth. Within this limited change zone, where the fraction remaining is near one, EDWCs based on deeper ASM depths would not change when compared 1-m ASM depth assumption.

The limited change zone varies with the zone of metabolism and the physical-chemical properties. For the 2m zone of metabolism (2m0x), an ASM half-life of 1000-days results in EDWCs that are 80 to 90% of the 1m0x assumption across the Koc values evaluated. For the 3m0x zone of metabolism, EDWCs are 80% to 90% of the 1m0x assumption for chemicals with a Koc of 500 and below but the percentage falls down to 60% between a Koc of 100 and 500 L/kg-oc.

The large change zone in **Figure D2** indicates the combinations of Koc (lower mobility, higher Koc) and ASM (shorter half-lives) where groundwater EDWCs are very sensitive to changes in ASM depth. Because of the length of time taken for rainfall to reach GW at the depth of the wells simulated, it would be expected that pesticides with shorter ASM half-lives would only occur at very low concentrations. When considering Koc values near or below 100 L/kg-oc, the large change zone occurs for ASM half-life values below 200-days. When considering Koc values of 500 L/kg-oc, the large change extends to ASM half-life values of 500-days, depending on the zone of ASM assumed.

Between the large and limited change zones is a transition zone where small changes in ASM half-life and Koc to a lesser extent would appear to have impactful changes to EDWCs for those chemicals that have long enough half-lives that they would be expected to occur in GW at concentrations that may potentially be of concern.

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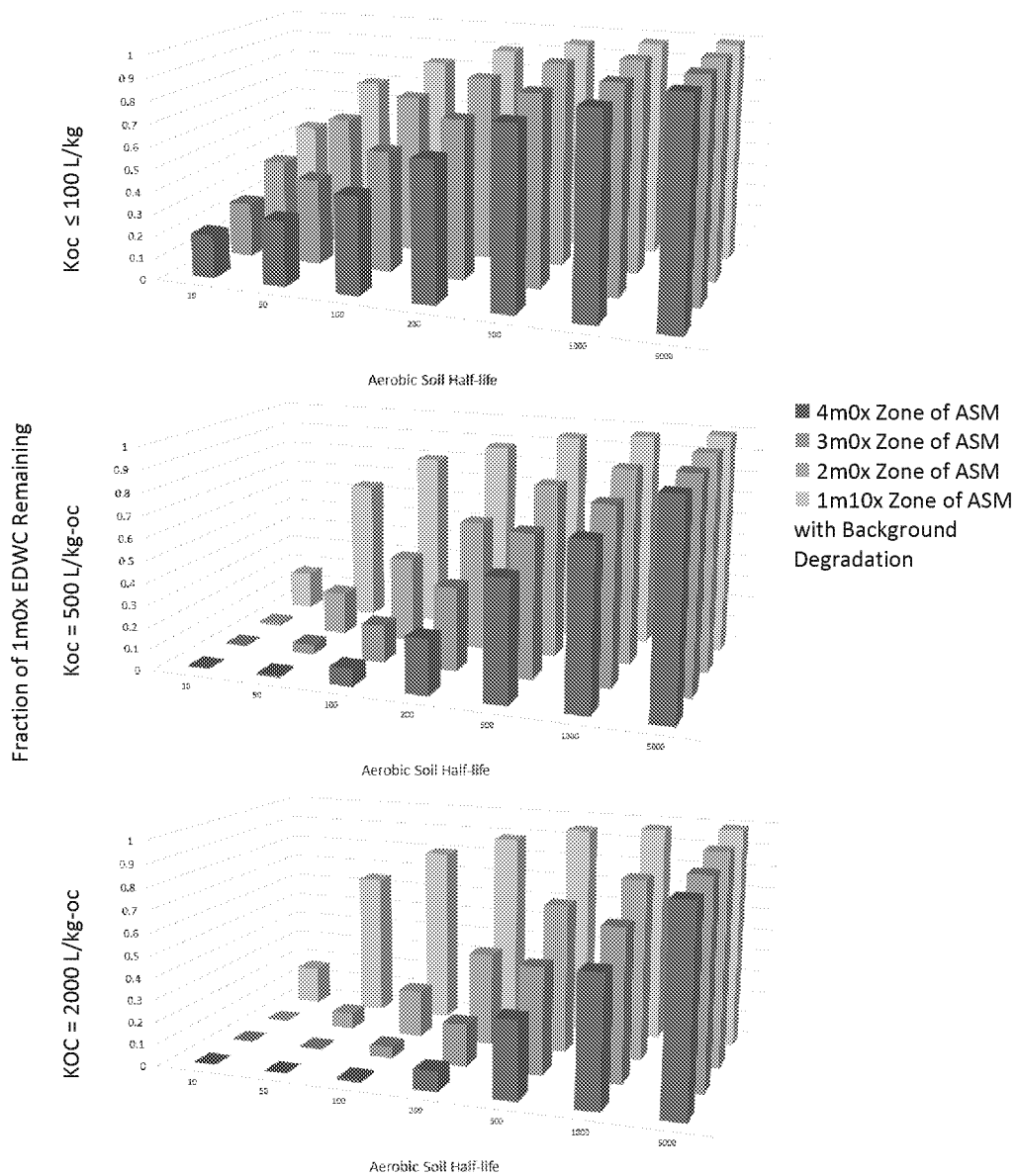


Figure D3. Impact of Changing Aerobic Soil Metabolism (ASM) Depth on EDWCs Across Koc and ASM Half-life

While **Figure D2** provides a comprehensive depiction of the variations in EDWCs with different ASM depth assumptions, it can be difficult to determine what the EDWC reduction would be for a chemical with a specific Koc and ASM half-life. To aid in this effort, **Table D1** provides a selection of EDWC reductions achieved at a specific set of ASM half-lives and Koc values for different ASM depths relative to the standard 1-meter ASM depth assumption. For example, using **Table D1**, it can be estimated that a chemical with a Koc near 0 and an ASM half-life of 10 days would have a peak EDWC that was approximately 20 to 36% of the 1-meter ASM depth EDWC, depending on the zone of metabolism assumed. However, such estimates are only true for chemicals with hydrolysis half-lives longer than the ASM half-life.

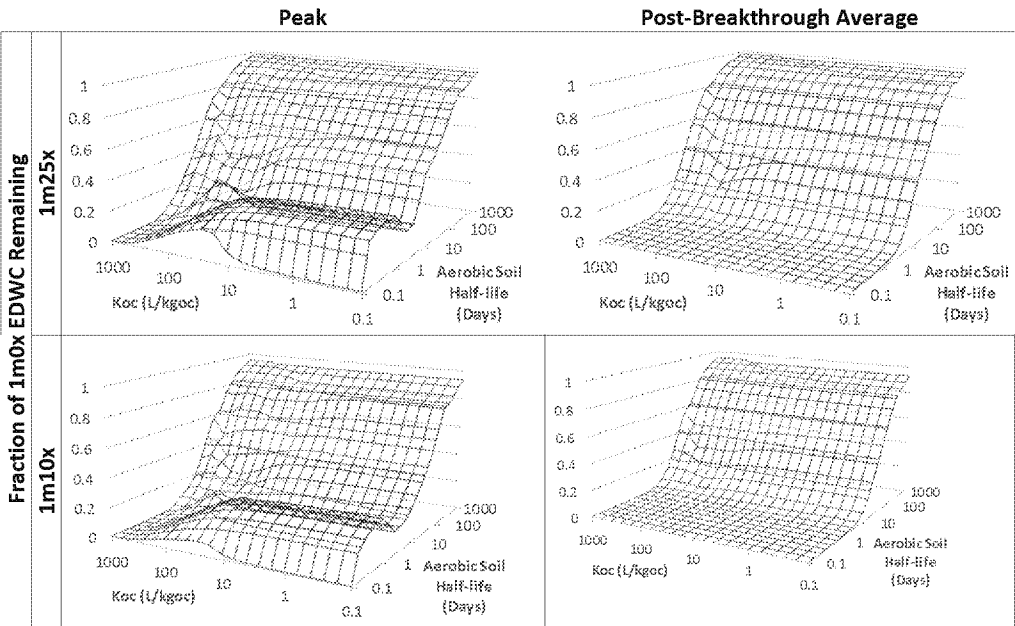
**Table D1. Variation in the Fraction of 1-meter ASM Depth Peak and PBA EDWC Remaining with Different Modeling Assumptions and Combinations of Koc and ASM half-life**

Modeling Assumption	ASM $T_{1/2}$ (days)	Fraction of 1m0x Peak EDWC Remaining (Post-Breakthrough Average)							
		Koc=0		Koc=100		Koc=500		Koc=1000	
2m0x	10	0.36	(0.16)	0.10	(0.07)	0.01	(<0.01)	<0.01	(<0.01)
	50	0.59	(0.58)	0.48	(0.45)	0.19	(0.18)	0.07	(0.07)
	100	0.72	(0.74)	0.62	(0.64)	0.39	(0.38)	0.21	(0.21)
	200	0.83	(0.86)	0.77	(0.79)	0.59	(0.59)	0.42	(0.42)
	500	0.92	(0.94)	0.90	(0.91)	0.79	(0.80)	0.67	(0.68)
	1000	0.96	(0.97)	0.95	(0.95)	0.88	(0.89)	0.81	(0.82)
	5000	0.99	(0.99)	0.99	(0.99)	0.98	(0.98)	0.96	(0.96)
3m0x	10	0.25	(0.03)	0.05	(0.01)	<0.01	(<0.01)	<0.01	(<0.01)
	50	0.39	(0.28)	0.25	(0.17)	0.04	(0.03)	0.01	(<0.01)
	100	0.55	(0.50)	0.44	(0.38)	0.17	(0.14)	0.05	(0.04)
	200	0.72	(0.70)	0.62	(0.60)	0.38	(0.35)	0.19	(0.18)
	500	0.86	(0.86)	0.82	(0.81)	0.65	(0.64)	0.48	(0.48)
	1000	0.93	(0.93)	0.90	(0.90)	0.80	(0.80)	0.68	(0.68)
	5000	0.98	(0.99)	0.98	(0.98)	0.96	(0.95)	0.92	(0.93)
4m0x	10	0.20	(0.01)	0.04	(<0.00)	<0.01	(<0.01)	<0.01	(<0.01)
	50	0.30	(0.21)	0.14	(0.10)	0.01	(0.01)	<0.01	(<0.01)
	100	0.44	(0.44)	0.31	(0.29)	0.08	(0.07)	0.01	(0.01)
	200	0.63	(0.65)	0.50	(0.53)	0.25	(0.24)	0.09	(0.09)
	500	0.81	(0.84)	0.75	(0.77)	0.54	(0.55)	0.35	(0.36)
	1000	0.90	(0.92)	0.86	(0.87)	0.73	(0.73)	0.58	(0.59)
	5000	0.98	(0.98)	0.97	(0.97)	0.94	(0.94)	0.89	(0.90)
1m10x	10	0.45	(0.15)	0.27	(0.13)	0.17	(0.12)	0.17	(0.11)
	50	0.69	(0.61)	0.67	(0.62)	0.64	(0.61)	0.65	(0.60)
	100	0.76	(0.78)	0.81	(0.78)	0.80	(0.77)	0.80	(0.78)
	200	0.86	(0.88)	0.91	(0.88)	0.88	(0.88)	0.89	(0.88)
	500	0.94	(0.95)	0.96	(0.95)	0.95	(0.95)	0.95	(0.95)
	1000	0.97	(0.97)	0.98	(0.97)	0.97	(0.97)	0.97	(0.98)
	5000	0.99	(0.99)	1.00	(0.99)	1.00	(0.99)	0.99	(1.00)



Section D3. Impact of Assuming a Background Degradation Rate on EDWCs

**Figure D4** is similar to **Figure D2**, except it compares the modeling assumption of a background metabolism rate as a fraction of the surface ASM rate in the dissolved phase (*i.e.*, changing the hydrolysis for pesticides that are stable to hydrolysis) to the 1m0x modeling assumption. Assuming a background metabolism rate resulted in smaller reductions in EDWCs as compared to changing the depth which ASM is assumed to occur (**Figure D2**). Two different assumptions were explored: 25× and 10× the ASM half-life. Note that 25× the ASM half-life results in a longer half-life and therefore slower degradation (less reduction in EDWCs in top row of **Figure D4**) than 10× the ASM half-life (greater reduction in bottom row of **Figure D4**).



**Figure D4. Impact of Assuming a Background Degradation Rate for Pesticides Stable to Hydrolysis**

Similar large, limited, and transition zones can be identified in these graphs, but with two major differences. First, these zones are shifted toward shorter ASM half-lives when compared to the zones in **Figure D2**. This is due to the more limited change produced by the hydrolysis input substitutions than changing the ASM depth. And second, because the hydrolysis input only pertains to dissolved phase degradation, where Koc does not impact degradation to the extent that it does when changing ASM depth.

Peak and PBA EDWCs with the 1m10x were 80 to 90% of the 1m0x EDWCs for ASM half-life values greater than 200-days and 60 to 70% for ASM half-life values of 50 and 100-days across

Koc values. The fraction of the 1m0x EDWCs for ASM half-life near 10-days decreases from 0.45 to 0.17 as the Koc value increases; however, these EDWCs also tend to be very low, even when the hydrolysis is assumed to be stable. The PBA EDWCs for the 10-day ASM range from 0.11 to 0.15 the 1m0x EDWCs.

#### Section D4. Impact Changing Model Assumptions to the EDWCs of the Monitored Chemicals Considered in this White Paper

The PWC modified assumptions are evaluated using two different sets of pesticides. The first is a set of pesticides referred to as the “PGW” chemicals because these are used in **Section 5** for comparisons to PGW study data. The PGW chemicals consist of 10 pesticides and are compared using EDWCs from only the GW scenario considered to be most like the soil/GW system studied in the PGW study and the application rate used in that PGW study.

The second set of 59 chemicals is referred to as the “WQP” pesticides and is compared in **Section 6** to the WQP monitoring data. The WQP modeling, reflecting 100-year simulation results) used are the highest EDWC produced using maximum labeled application rates by any of the six standard GW scenarios typically used by EFED in drinking water assessments (*i.e.*, the EDWC typically recommended in DWAs). Note that all the PGW chemicals are included as a subset of the WQP chemicals. However, the PGW and WQP EDWCs differ for the same pesticide due to differences in the assumed application rates, 30-year simulations for the PGW analysis, and only simulating one PWC scenario in the PGW analysis.

Separate PWC batch input files were created to complete model simulations. Each batch file was run 12 times (the current modeling assumptions and the 11 potential refinement options) – once for each combination of declining ASM with depth (*i.e.*, 1, 2, 3, and 4m) and factor of the ASM half-life that was invariant with depth (*i.e.*, 0x, 10x, and 25x) entered in the hydrolysis input.

The background degradation rate assumptions require substituting a 10 times or 25 times the ASM half-life into the abiotic hydrolysis input and is not applicable for chemicals that are not stable to abiotic hydrolysis. For all of the chemicals that underwent abiotic hydrolysis, the hydrolysis half-life was faster than 10x or 25x the ASM half-life. Because two of the 10 PGW and 17 of the 59 WQP chemicals undergo hydrolysis, these pesticides are not included in the analyses involving the 10x and 25x refinements. Therefore, there are only 9 PGW and 42 WQP pesticides presented for the 10x and 25x refinements. Graphical presentation of this analysis is in [ REF\_Ref36561242 \h \\* MERGEFORMAT ].

**Table D2** categorizes the number and percentage of chemicals analyzed that fall into different categories of magnitude of EDWC change with each modeling assumption. Note that a pesticide may occupy a different category with different modeling assumptions. This table is split between those modified assumptions that could be performed on all pesticides (**Table D2a**) and the entire set of assumptions that could be performed on the smaller sets of PGW and WQP chemicals (**Table D2b**). For example, looking at PBA EDWCs only, when the ASM transformation

[ PAGE \\* MERGEFORMAT ]

zone was increased from 1 m to 2 m (2m0x) none (0%) of the 11 chemicals had a reduction in the EDWCs greater than 100x. **Table D2** illustrates that for the PGW simulations modeled modifications were within a factor of 10x the standard EDWCs. When increased in the zone of metabolism 60 to 100% of the EDWCs were within a factor of 10x the 1m0x modeling assumption.

There was limited reduction in the EDWCs for the 25x ASM half-life assumption as the background degradation rate. Therefore, this modeling assumption was not explored further.

**Table D2. Summary of Reduction in Modified Modeling EDWC as Compared to the Standard Modeling EDWCs for Peak and Post-breakthrough Average (PBA) Concentrations**

(a) Zone of Aerobic Soil Metabolism

Refinement	Number of Pesticides (Percent of Pesticides)					
	<10x Lower		10x to 100x Lower		>100x Lower	
	Peak	PBA	Peak	PBA	Peak	PBA
Prospective Groundwater Simulations (N = 11)						
2m0x	10 (91%)	10 (91%)	1 (9%)	1 (9%)	0 (0%)	0 (0%)
3m0x	9 (82%)	9 (82%)	1 (9%)	1 (9%)	1 (9%)	1 (9%)
4m0x	9 (82%)	8 (73%)	0 (0%)	1 (9%)	2 (18%)	2 (18%)
Water Quality Portal Pesticides (N = 59)						
2m0x	50 (85%)	48 (81%)	6 (10%)	7 (12%)	3 (5%)	4 (7%)
3m0x	45 (76%)	43 (73%)	7 (12%)	6 (10%)	7 (12%)	10 (17%)
4m0x	40 (68%)	35 (59%)	11 (19%)	12 (20%)	8 (14%)	12 (20%)

(a) Zone of Aerobic Soil Metabolism and Assuming the Hydrolysis Input is 25 or 10x ASM

Refinement	Number of Chemicals (Percent of Pesticides)					
	<10x Lower		10x to 100x Lower		>100x Lower	
	Peak	PBA	Peak	PBA	Peak	PBA
Prospective Groundwater Pesticides (N = 9)						
2m0x	9 (100%)	9 (100%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
3m0x	8 (89%)	8 (89%)	1 (11%)	1 (11%)	0 (0%)	0 (0%)
4m0x	8 (89%)	7 (78%)	0 (0%)	1 (11%)	1 (11%)	1 (11%)
1m25x	9 (100%)	9 (100%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
2m25x	9 (100%)	9 (100%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
3m25x	8 (89%)	8 (89%)	1 (11%)	1 (11%)	0 (0%)	0 (0%)
4m25x	8 (89%)	7 (78%)	0 (0%)	1 (11%)	1 (11%)	1 (11%)
1m10x	9 (100%)	9 (100%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
2m10x	9 (100%)	9 (100%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
3m10x	8 (89%)	8 (89%)	1 (11%)	1 (11%)	0 (0%)	0 (0%)
4m10x	8 (89%)	7 (78%)	0 (0%)	1 (11%)	1 (11%)	1 (11%)
Water Quality Portal Chemicals (N = 42)						
2m0x	38 (90%)	36 (86%)	2 (5%)	3 (7%)	2 (5%)	3 (7%)
3m0x	33 (79%)	33 (79%)	6 (14%)	4 (10%)	3 (7%)	5 (12%)
4m0x	30 (71%)	26 (62%)	8 (19%)	9 (21%)	4 (10%)	7 (17%)
1m25x	40 (95%)	40 (95%)	1 (2%)	0 (0%)	1 (2%)	2 (5%)
2m25x	36 (86%)	35 (83%)	3 (7%)	3 (7%)	3 (7%)	4 (10%)
3m25x	33 (79%)	33 (79%)	6 (14%)	3 (7%)	3 (7%)	6 (14%)
4m25x	30 (71%)	26 (62%)	8 (19%)	9 (21%)	4 (10%)	7 (17%)
1m10x	40 (95%)	36 (86%)	1 (2%)	4 (10%)	1 (2%)	2 (5%)
2m10x	36 (86%)	34 (81%)	3 (7%)	4 (10%)	3 (7%)	4 (10%)

[ PAGE \\* MERGEFORMAT ]

Refinement	Number of Chemicals (Percent of Pesticides)					
	<10× Lower		10× to 100× Lower		>100× Lower	
	Peak	PBA	Peak	PBA	Peak	PBA
3m10×	33 (79%)	33 (79%)	6 (14%)	2 (5%)	3 (7%)	7 (17%)
4m10×	28 (67%)	26 (62%)	10 (24%)	9 (21%)	4 (10%)	7 (17%)

PBA = Post breakthrough average

[ PAGE \\* MERGEFORMAT ]

## Appendix [ SEQ Appendix \\* ALPHABETIC ], Selection and Properties of Chemicals Analyzed in the Modeling

In order to evaluate whether the model modifications (changing the zone of ASM) or changes in modeling inputs assumptions (assuming the hydrolysis half-life was 10 times or 25 times the ASM input) would be reasonable and conservative, predicted EDWCs from modeling were compared with results from monitoring. Monitoring results from PGW monitoring studies were utilized to evaluate how well the PWC simulations with modifications matched actual measured concentrations in the field. In this evaluation, model assumptions are matched to the PGW study. Additionally, GW monitoring results from the WQP, were utilized to understand results across a wider range of pesticides,

The PGW monitoring analysis pesticides were selected based on having a readily available PGW study. For the WQP monitoring analysis, pesticides previously evaluated in the PRZM-GW evaluation work, both completed in the evaluation of GW models[ ADDIN EN.CITE

<EndNote><Cite><Author>USEPA</Author><Year>2012</Year><RecNum>5244</RecNum><DisplayText><style face="superscript">1</style></DisplayText><record><rec-number>5244</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1535036560" guid="5462a21c-9e46-4eb3-bef7-2381d1408413">5244</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>USEPA,</author><author>Health Canada,</author></authors></contributors><titles><title>Identification and Evaluation of Existing Models for Estimating Environmental Pesticide Transport to Groundwater</title><secondary-title>October 15, 2012</secondary-title><tertiary-title>Environmental Fate and Effects Division. Office of Pesticide Programs. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2012</year></dates><urls></urls></record></Cite></EndNote>

and the analysis on implementation of PRZM-GW[ ADDIN EN.CITE

<EndNote><Cite><Author>USEPA</Author><Year>2015</Year><RecNum>5243</RecNum><DisplayText><style face="superscript">6</style></DisplayText><record><rec-number>5243</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1535036345" guid="be2c7578-9a21-4123-a098-2fcef3184d36">5243</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>USEPA</author></authors></contributors><titles><title>Implementation of the Pesticide Root Zone Model Groundwater (PRZM-GW) for Use in EPA's Pesticide Exposure Assessments</title><secondary-title>September 8, 2015</secondary-title><tertiary-title>Environmental Fate and Effects Division. Office of Pesticide Programs. U.S. Environmental Protection Agency</tertiary-title></titles><dates><year>2015</year></dates><urls></urls></record></Cite></EndNote>

were used as a starting list along with the pesticides with both subsurface and surface ASM data. Pesticides commonly found in GW or that may have previously needed GW modeling refinements were also considered in the analysis[ ADDIN EN.CITE

[ PAGE \\* MERGEFORMAT ]

<EndNote><Cite><Author>Toccalino</Author><Year>2014</Year><RecNum>5314</RecNum><DisplayText><style face="superscript">57</style></DisplayText><record><rec-number>5314</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184602" guid="07061e8e-6ab9-4ac5-bc39-d33fe5b25213">5314</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Toccalino, Patricia L.</author><author>Gilliom, Robert J.</author><author>Lindsey, Bruce D.</author><author>Rupert, Michael G.</author></authors></contributors><titles><title>Pesticides in Groundwater of the United States: Decadal-Scale Changes, 1993–2011</title></titles><pages>112-125</pages><volume>52</volume><number>S1</number><dates><year>2014</year></dates><isbn>0017-467X</isbn><urls><related-urls><url>https://ngwa.onlinelibrary.wiley.com/doi/abs/10.1111/gwat.12176</url></related-urls></urls><electronic-resource-num>10.1111/gwat.12176</electronic-resource-num></record></Cite></EndNote>]. This resulted in a list of 77 pesticides for potential analysis. Pesticides that were stable to both hydrolysis and ASM were removed from the final analysis, as the model modifications would not impact these pesticides. Some pesticides were also eliminated because WQP data were not available.

**Table E1** summarizes the persistence classifications based on the ASM half-life using the Goring scale[ ADDIN EN.CITE

<EndNote><Cite><Author>Goring</Author><Year>1975</Year><RecNum>1070</RecNum><DisplayText><style face="superscript">77</style></DisplayText><record><rec-number>1070</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1407523667" guid="55916049-9403-473d-bce7-570aee1ea2d7">1070</key></foreign-keys><ref-type name="Book Section">5</ref-type><contributors><authors><author>Goring, C.A.I.</author><author>Laskowski, D. A.</author><author>Hamaker, J. H.</author><author>Meikle, R.W.</author></authors><secondary-authors><author>Haque, R.</author><author>Freed, V.H.</author></secondary-authors></contributors><titles><title>Principles of pesticide degradation in soil.</title><secondary-title>Environmental dynamics of pesticides.</secondary-title></titles><dates><year>1975</year></dates><pub-location>NY</pub-location><publisher>Plenum Press</publisher><urls><related-urls><url>https://link.springer.com/chapter/10.1007%2F978-1-4684-2862-9\_9</url></related-urls></urls></record></Cite></EndNote>] and the Food and Agricultural Organization (FAO) mobility classification of the final chemicals that were evaluated. The moderately mobile class was split into two groups (100-499 L/kg-organic carbon and 500-1000 L/kg-organic carbon) to better understand the influence of mobility on results. A full list of chemicals analyzed along with the assumed model inputs is provided in **Table E3 and Table E4**.

**Table E1. Summary of the Persistence and Mobility of Water Quality Portal and Prospective Groundwater Study Pesticides for Changing the Zone of Degradation<sup>4</sup>**

Mobility Category <sup>3</sup>	Number of Pesticides by Persistence Category <sup>2</sup>				Grand Total
	Non-persistent <15 days	Slightly Persistent 15-45 days	Moderately Persistent 45-180 days	Persistent >180 days	
<10 highly Mobile	1	1	1	1	4
10-100 Mobile	4	3	7 (3)	9 (3)	23
100-499 Moderately Mobile	5	1	9 (2)	3 (1)	18
500-1000 Moderately Mobile	1	2	1 (1)	8	12
1000-4000 slightly Mobile	--	--	--	2	2
Grand Total	11	7	18	23	59

<sup>1</sup> The number of prospective groundwater monitoring study chemicals evaluated is shown in parentheses.

<sup>2</sup> The persistence category applies to the aerobic soil half-life for the surface using the Goring persistence scale[ ADDIN EN.CITE

<EndNote><Cite><Author>Goring</Author><Year>1975</Year><RecNum>1070</RecNum><DisplayText><style face="superscript">77</style></DisplayText><record><rec-number>1070</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1407523667" guid="55916049-9403-473d-bce7-570aee1ea2d7">1070</key></foreign-keys><ref-type name="Book Section">5</ref-type><contributors><authors><author>Goring, C.A.I.</author><author>Laskowski, D. A.</author><author>Hamaker, J. H.</author><author>Meikle, R.W.</author></authors><secondary-authors><author>Haque, R.</author><author>Freed, V.H.</author></secondary-authors></contributors><titles><title>Principles of pesticide degradation in soil.</title><secondary-title>Environmental dynamics of pesticides. </secondary-title></titles><dates><year>1975</year></dates><pub-location>NY</pub-location><publisher>Plenum Press</publisher><urls><related-urls><url>https://link.springer.com/chapter/10.1007%2F978-1-4684-2862-9\_9</url></related-urls></urls></record></Cite></EndNote>].

<sup>3</sup> The FAO mobility scale[ ADDIN EN.CITE

<EndNote><Cite><Author>FAO</Author><Year>2000</Year><RecNum>83</RecNum><DisplayText><style face="superscript">78</style></DisplayText><record><rec-number>83</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1247233164" guid="affd17f7-78d7-42c6-a1da-6ca07c7339fc">83</key><key app="ENWeb" db-id="RcJqaQrtmCQAAFU55fA">558</key></foreign-keys><ref-type name="Book Section">5</ref-type><contributors><authors><author>FAO</author></authors><secondary-authors><author>FAO Information Division Editorial Group,</author></secondary-authors></contributors><titles><title>Appendix 2. Parameters of pesticides that influence processes in the soil</title><secondary-title>Pesticide Disposal Series 8. Assessing Soil Contamination. A Reference Manual</secondary-title></titles><dates><year>2000</year></dates><pub-location>Rome</pub-location><publisher>Food & Agriculture Organization of the United Nations (FAO)</publisher><urls><related-urls><url>http://www.fao.org/DOCREP/003/X2570E/X2570E06.htm</url></related-urls></urls></record></Cite></EndNote>] was used to categorize the mobility of the chemicals evaluated; however, the Moderately Mobile classification was split into two groups for better resolution.

<sup>4</sup> This table includes chemicals with throughputs greater than one in at least one PWC scenario when simulating 100-years of data.

For the pesticides with throughputs greater than one in at least one PWC scenario, 59 different chemicals were evaluated in the WQP analysis, 42 of which were stable to hydrolysis. See **Table E2**, for a breakdown of chemicals included in these analyses.

**Table E2. Summary of the Persistence and Mobility of Water Quality Portal and Prospective Groundwater Study Pesticides Evaluated for Assuming Changes to the Hydrolysis Input<sup>4</sup>**

Mobility Category <sup>3</sup>	Number of Pesticides by Persistence Category <sup>2</sup>				Grand Total
	Non-persistent <15 days	Slightly Persistent 15-45 days	Moderately Persistent 45-180 days	Persistent >180 days	
<10 highly Mobile	1	1	1	1	4
10-100 Mobile	3	7	2 (2)	4 (2)	16
100-499 Moderately Mobile	3	3	1 (2)	5 (1)	12
500-1000 Moderately Mobile	--	7	1 (1)	1	9
1000-4000 slightly Mobile	-	1	--	--	1
Grand Total	7	19	5	11	42

<sup>1</sup> The number of prospective groundwater monitoring study chemicals in evaluated is shown in parentheses.

<sup>2</sup> The persistence category applies to the aerobic soil half-life for the surface using the Goring persistence scale[ ADDIN EN.CITE

<EndNote><Cite><Author>Goring</Author><Year>1975</Year><RecNum>1070</RecNum><DisplayText><style face="superscript">77</style></DisplayText><record><rec-number>1070</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1407523667" guid="55916049-9403-473d-bce7-570aee1ea2d7">1070</key></foreign-keys><ref-type name="Book Section">5</ref-type><contributors><authors><author>Goring, C.A.I.</author><author>Laskowski, D. A.</author><author>Hamaker, J. H.</author><author>Meikle, R.W.</author></authors><secondary-authors><author>Haque, R.</author><author>Freed, V.H.</author></secondary-authors></contributors><titles><title>Principles of pesticide degradation in soil.</title><secondary-title>Environmental dynamics of pesticides. </secondary-title></titles><dates><year>1975</year></dates><pub-location>NY</pub-location><publisher>Plenum Press</publisher><urls><related-urls><url>https://link.springer.com/chapter/10.1007%2F978-1-4684-2862-9\_9</url></related-urls></urls></record></Cite></EndNote>].

<sup>3</sup> The FAO mobility scale[ ADDIN EN.CITE

<EndNote><Cite><Author>FAO</Author><Year>2000</Year><RecNum>83</RecNum><DisplayText><style face="superscript">78</style></DisplayText><record><rec-number>83</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1247233164" guid="affd17f7-78d7-42c6-a1da-6ca07c7339fc">83</key><key app="ENWeb" db-id="RcJqaQrtmCQAAFU55fA">558</key></foreign-keys><ref-type name="Book Section">5</ref-type><contributors><authors><author>FAO</author></authors><secondary-authors><author>FAO Information Division Editorial Group,</author></secondary-authors></contributors><titles><title>Appendix 2. Parameters of pesticides that influence processes in the soil</title><secondary-title>Pesticide Disposal Series 8. Assessing Soil Contamination. A Reference Manual</secondary-title></titles><dates><year>2000</year></dates><pub-location>Rome</pub-location><publisher>Food & Agriculture Organization of the United Nations (FAO)</publisher><urls><related-urls><url>http://www.fao.org/DOCREP/003/X2570E/X2570E06.htm</url></related-urls></urls></record></Cite></EndNote>] was used to categorize the mobility of the chemicals evaluated; however, the Moderately Mobile classification was split into two groups for better resolution.

<sup>4</sup> This table includes chemicals with throughputs greater than one in at least one PWC scenario when simulating 100-years of data. The chemicals considered for evaluating changes in the hydrolysis inputs were fewer because only chemicals that were stable to hydrolysis could be included in this analysis.

For the PGW analysis, nine pesticides and one degradate were evaluated. These pesticides were mobile to moderately mobile and moderately persistent to persistent. The chemicals evaluated in the PGW analysis were also evaluated in the WQP analysis, except for acetochlor ethanesulfonic acid. Acetochlor parent was examined in the WQP analysis and acetochlor



ethanesulfonic acid was examined in the PGW analysis. Chemicals in the slightly mobile category and with organic carbon normalized soil-water distribution coefficients ( $K_{oc}$ ) values greater than 1500 L/kg-organic carbon did not have throughputs greater than one in all scenario simulations.

In Section [ REF\_Ref37171928 \r \h \\* MERGEFORMAT ] (the evaluation of the impacts of the model modifications) chemicals with a  $K_{oc}$  greater than 1500 L/kg were not included in the analysis. In Section [ REF\_Ref36382537 \r \h \\* MERGEFORMAT ], comparison of the modeling to the WQP monitoring results, data were characterized for simulations that resulted in throughputs greater than one for chemicals with  $K_{oc}$  values greater than 1500 L/kg-oc. Additionally, some chemicals with GW monitoring results that did not have throughputs greater than one in any of the simulations were also discussed separately. These were in addition to the 59 chemicals summarized in Table E1 and Table E2.

Table E3. Summary of Chemicals Analyzed in the Modeling and Water Quality Portal Data Analysis (Chemicals with Throughputs Greater than 1 in at least 1 PWC scenario)

Chemical	Mean $K_{oc}$ (L/kg-oc) <sup>1</sup>	Hydrolysis Half-Life (days)	Soil Half-life Input (days)	Max WQP Concentration in GW $\mu\text{g/L}$		Single App Rate (kg/ha)
				All Samples	Dissolved	
2,4-D	$K_{oc}=0.52$	0	6.92	24	14.8	2.24
Acetochlor	133	0	13.3	8.2	0.77	1.68
Acifluorfen	109	0	173	0.9	0.9	2.24
Alachlor	86	0	42	47.3	47.3	4.48
Aldicarb	0.33	0	8.47	180	0.239	2.774
Aminopyralid	8.96	0	98.8	0.103		0.12
Atrazine	75	0	139	270	20	1.12
Azinphos-methyl	8.414	37	95	0.432		2
Bentazon	0.898	1197	48.97	120	0.432	1.68
Bromacil	41.1	0	275	57	11.5	4.8
Butylate	247	0	71.7	0.7	57	6.83
Carbaryl	211	12	176	4.42	0.7	13.6
Carbofuran	30	28	321	21	4.42	1.12
Chloropicrin	36.05	0	0.9	0.645	2.16	118.14
Clopyralid	0.4	0	109	22.6	22.6	0.28
cyanazine	84	0	61.8	76	6.93	5.6
Cycloate	562	0	38.4	0.8	0.07	4.48
Diazinon	758	138	123.3	490	19	3.36
Dichlobenil	237	0	972	0.41	0.41	22.4
Dichlorprop	69	0	42	0.7	0.7	8.43
Disulfoton	552	300	20	0.109	0.109	1
Diuron	463	0	1116	5.8	5.8	8.96
Fenamiphos	0.958	300	47.1	0.71	0.497	6.16
Fipronil	727	2140	349.4	0.43	0.43	0.366
Flumetsulam	27.3	0	98.9	0.803	0.297	0.078
Fluometuron	56.5	0	543	4.7	4.7	2.24
Flutolanil	780.7	0	435.1	0.22		9.64
Glyphosate	157	0	29	280	280	3.73
Imazapyr	99.8	0	0	0.162		0.84
Imazaquin	17.5	0	630	0.7	0.7	0.56

[ PAGE \\* MERGEFORMAT ]

Chemical	Mean K <sub>oc</sub> (L/kg-oc) <sup>1</sup>	Hydrolysis Half-Life (days)	Soil Half-life Input (days)	Max WQP Concentration in GW µg/L		Single App Rate (kg/ha)
				All Samples	Dissolved	
Imidacloprid	266	0	254	4.48	4.48	0.56
Iprodione	426	4.7	48	0.016	0.016	4
Isofenphos	972	0	1056	0.023	0.023	2
Lindane	1368	0	2940	17	0.47	0.13
Linuron	2000	1139	628	18	18	2.25
Malathion	151	100	3	25	0.88	7.84
Metaxyl	409	200	419	7.33	7.33	4.48
Metolachlor	181	0	49	210	210	4.48
Metribuzin	32	0	318	8.2	8.2	6
Metsulfuron-methyl	7.7	0	31	0.23	0.23	0.028
Myclobutanil	224	0	251	1.42	1.42	0.28
Napropamide	577	0	1338	0.137	0.137	4
Norflurazon	0.14	0	390	26.5	26.5	8.96
Oryzalin	941	0	189	1.18	1.18	6.72
Oxamyl	35	8	35	23	23	2.2
Parathion-methyl	486	40	11	1.6	0.08	0.74
Pebulate	400	0	180	0.116	0.116	10
Prometon	118	0	1423	40	40	67.18
Propachlor	112	0	8.1	0.8	0.112	8.72
Propanil	851	0	0.5	0.219	0.219	8.96
Propazine	125	0	480	3.41	3.41	1.34
Propiconazole	648	0	69	0.125	0.125	0.225
Simazine	123.25	0	128.3	26.5	22	1.12
Sulfentrazone	29	375	552	0.26	0.26	0.56
Tebuthiuron	85	0	270.6	17.3	17.3	6.72
Telone	41	13.5	97.6	579	--	841
Terbacil	54	0	653	2.68	2.68	2
Terbufos	1448	15	81	20	0.36	4
Thiamethoxam	70.23	0	236	6.34	6.34	0.29

GW=groundwater; WQP=Water Quality Portal; App=Application; Max=maximum

<sup>1</sup> Units of soil-water distribution coefficients are provided in L/kg-soil. Units of organic-carbon normalized soil-water distribution coefficients are provided in units of L/kg-organic carbon.

Appendix [SEQ Appendix \\* ALPHABETIC]. Supporting Material for  
Prospective Groundwater Modeling Analyses

Table F1. Input data for 30-year and 10-year PGW modeling

Chemical	GW Scenario	K <sub>oc</sub> (L/kg-oc)	Hydrolysis (days)	Soil Half-life (days)	PGW Location	MRID (unless otherwise specified)
Fenamiphos	FL Central Ridge	K <sub>d</sub> = 0.958	300	47.1	Central Highlands Ridge, FL	44505401
AcetochlorESA	Delmarva	28.8	0	106	Delaware	DP Barcode 292329
AcetochlorESA	WI sands	28.8	0	106	Wisconsin	DP Barcode 292329
Acifluorfen	WI sands	109	0	173	Wisconsin	41172801
Bromacil	FL Central Ridge	41.1	0	275	Central Ridge, FL	44480701
Imidacloprid	WI sands	266	0	254	Vestaburg (Montcalm), MI	45858201
Metribuzin	WI sands	20	0	73.7	Portage County, WI	49013301
Metolachlor	GA	132.4	0	98.4	Macon County, GA	47017401
Norflurazon	FL Central Ridge	776	0	138	Central Highlands Ridge, FL	45630701
Thiamethoxam	WI sands	70.23	0	236	St. Joseph, MI	47486201
Sulfentrazone	NC Coastal Plain	29	375	552	Edgecombe County, NC	43345434, 43926814

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Table E2. Output for 30-year PGW modeling

30 Years PGW Analysis	GW Scenario	PGW Max	1m0x			1m10x			1m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos-FL	FLCitrus	0.58	26	21	13						
AcetochlorESA-NJ	Delmarva	3.1	336	271	223	255	203	168	300	241	199
AcetochlorESA-WI	Wlcorn	10.7	387	349	268	269	226	175	334	293	225
Acifluorfen_WI	Wlcorn	46	154	142	98	120	109	76	139	128	89
Bromacil-FL	FLCitrus	55	384	305	275	331	258	233	362	285	257
Imidacloprid_WI	Wlcorn	0.24	65	60	34	55	50	29	60	56	32
Metribuzin_WI	Wlcorn	5.9	180	158	122	111	89	69	148	125	97
Metolachlor_GA	GA peanuts	0.78	83	76	57	50	44	33	68	61	45
Norflurazon_FL	FLCitrus	26	159	158	82	128	124	66	145	143	75
Thiamethoxam_WI	Wlcorn	0.16	43	39	29	36	32	24	40	36	26
Sulfentrazone_NC	NCCotton	37.4	37	22	18						

30 Years PGW Analysis	GW Scenario	PGW Max	2m0x			2m10x			2m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos	FLCitrus	0.58	1.13	0.76	0.53						
AcetochlorESA	Delmarva	3.1	215	176	145	192	153	126	212	171	141
AcetochlorESA	Wlcorn	10.7	291	257	197	226	189	145	281	244	188
Acifluorfen	Wlcorn	46	120	110	76	101	91	63	116	107	74
Bromacil	FLCitrus	55	277	226	204	266	211	190	272	220	198
Imidacloprid	Wlcorn	0.24	50	46	26	44	40	23	49	45	26
Metribuzin	Wlcorn	5.6	125	107	83	90	71	55	120	100	78
Metolachlor	GA peanuts	0.78	38	35	26	27	24	18	36	33	25
Norflurazon	FLCitrus	26	19	19	11	18	17	10	19	18	11
Thiamethoxam	Wlcorn	0.16	36	33	24	32	29	21	36	32	24
Sulfentrazone	NCCotton	37.4	36	22	18						

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30 Years PGW Analysis	GW Scenario	PGW Max	3m0x			3m10x			3m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos	FLCitrus	0.58	0.13	0.08	0.05						
AcetochlorESA	Delmarva	3.1	148	123	101	144	115	95	146	120	99
AcetochlorESA	Wlcorn	10.7	227	195	150	211	175	135	224	191	147
Acifluorfen	Wlcorn	46	97	88	61	92	82	57	96	86	60
Bromacil	FLCitrus	55	203	167	151	196	156	141	200	163	147
Imidacloprid	Wlcorn	0.24	40	36	21	38	35	20	39	36	21
Metribuzin	Wlcorn	5.6	91	76	59	83	66	51	90	74	57
Metolachlor	GA peanuts	0.78	18	16	13	16	14	11	18	16	12
Norflurazon	FLCitrus	26	3.67	3.56	2.1	3.4	3.26	1.93	3.56	3.43	2.03
Thiamethoxam	Wlcorn	0.16	32	29	21	30	27	20	31	28	21
Sulfentrazone	NCCotton	37.4	36	22	18						

30 Years PGW Analysis	GW Scenario	PGW Max	4m0x			4m10x			4m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos	FLCitrus	0.58	0.06	0.02	0.01						
AcetochlorESA	Delmarva	3.1	111	88	73	107	83	68	109	86	71
AcetochlorESA	Wlcorn	10.7	180	150	116	173	141	109	177	147	113
Acifluorfen	Wlcorn	46	80	71	49	77	68	47	79	70	48
Bromacil	FLCitrus	55	158	122	111	158	122	111	158	122	111
Imidacloprid	Wlcorn	0.24	32	29	17	31	28	16	32	29	17
Metribuzin	Wlcorn	5.6	67	54	42	65	50	39	66	53	41
Metolachlor	GA peanuts	0.78	9.04	7.54	5.91	8.72	7.16	5.61	8.91	7.39	5.79
Norflurazon	FLCitrus	26	1.05	0.85	0.52	1.05	0.85	0.52	1.05	0.85	0.52
Thiamethoxam	Wlcorn	0.16	27	25	18	27	24	18	27	25	18
Sulfentrazone	NCCotton	37.4	36	22	18						

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Table E3. Output for 10-year PGW modeling

10 Year PGW Analysis	GW Scenario	PGW Max	1m0x			1m10x			1m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos-FL	FLCitrus	0.58	2.91	2.18	1.46						
AcetochlorESA-NJ	Delmarva	3.1	92	31	28	78	23	21	86	28	25
AcetochlorESA-WI	Wlcorn	10.7	87	42	35	56	27	22	72	35	29
Acifluorfen_WI	Wlcorn	46	24	12	9.66	18	9.03	7.44	22	11	8.7
Bromacil-FL	FLCitrus	55	111	29	29	101	24	25	106	27	27
Imidacloprid_WI	Wlcorn	0.24	8.13	6.52	4.16	6.86	5.41	3.48	7.6	6.05	3.87
Metribuzin_WI	Wlcorn	5.6	42	19	16	21	10	8.66	31	15	12
Metolachlor_GA	GA peanuts	0.78	14	5.61	4.84	9.08	3.31	2.94	12	4.53	3.96
Norflurazon_FL	FLCitrus	26	19	18	10	15	14	8.2	17	16	9.38
Thiamethoxam_WI	Wlcorn	0.16	8.34	3.68	3.09	6.69	3.02	2.55	7.64	3.4	2.86
Sulfentrazone_NC	NCCotton	37.4	10	2.98	2.84						

10 Year PGW Analysis	GW Scenario	PGW Max	2m0x			2m10x			2m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos	FLCitrus	0.58	0.14	0.08	0.06						
AcetochlorESA	Delmarva	3.1	71	20	18	66	18	16	70	20	18
AcetochlorESA	Wlcorn	10.7	66	30	25	45	22	18	62	29	24
Acifluorfen	Wlcorn	46	18	8.93	7.31	16	7.38	6.08	18	8.66	7.1
Bromacil	FLCitrus	55	90	21	22	87	20	20	89	21	21
Imidacloprid	Wlcorn	0.24	6.38	4.93	3.14	5.66	4.31	2.76	6.26	4.82	3.07
Metribuzin	Wlcorn	5.6	29	12	10	18	8.07	6.81	27	12	9.68
Metolachlor	GA peanuts	0.78	6.53	2.35	2.05	4.74	1.63	1.46	6.24	2.23	1.95
Norflurazon	FLCitrus	26	2.55	2.2	1.34	2.37	2.03	1.24	2.48	2.13	1.3
Thiamethoxam	Wlcorn	0.16	7	3.08	2.59	6.01	2.68	2.26	6.86	3.01	2.53
Sulfentrazone	NCCotton	37.4	10	2.94	2.81						

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10 Year PGW Analysis	GW Scenario	PGW Max	3m0x			3m10x			3m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos	FLCitrus	0.58	0.02	0.008	0.006						
AcetochlorESA	Delmarva	3.1	58	14	13	56	13	12	57	14	13
AcetochlorESA	Wlcorn	10.7	48	23	19	43	20	17	47	22	19
Acifluorfen	Wlcorn	46	15	7.04	5.79	14	6.59	5.44	15	6.94	5.72
Bromacil	FLCitrus	55	76	16	16	73	15	15	75	15	16
Imidacloprid	Wlcorn	0.24	5.14	3.88	2.48	4.93	3.7	2.37	5.09	3.84	2.45
Metribuzin	Wlcorn	5.6	20	8.62	7.24	17	7.39	6.23	19	8.32	7.01
Metolachlor	GA peanuts	0.78	3.24	1.08	0.98	2.96	0.96	0.87	3.19	1.06	0.95
Norflurazon	FLCitrus	26	0.57	0.47	0.27	0.53	0.44	0.25	0.55	0.46	0.26
Thiamethoxam	Wlcorn	0.16	5.89	2.64	2.22	5.64	2.52	2.12	5.85	2.62	2.2
Sulfentrazone	NCCotton	37.4	10	2.92	2.79						

10 Year PGW Analysis	GW Scenario	PGW Max	4m0x			4m10x			4m25x		
			Peak	PBA	Sim Avg	Peak	PBA	Sim Avg	Peak	PBA	Sim Avg
Fenamiphos	FLCitrus	0.58	0.007	0.001	0.0009						
AcetochlorESA	Delmarva	3.1	47	10	9.42	46	9.78	8.78	47	10	9.16
AcetochlorESA	Wlcorn	10.7	36	17	15	34	16	14	35	17	14
Acifluorfen	Wlcorn	46	12	5.62	4.64	12	5.43	4.5	12	5.54	4.58
Bromacil	FLCitrus	55	64	11	12	64	11	12	64	11	12
Imidacloprid	Wlcorn	0.24	4.17	3.08	1.98	4.09	3	1.93	4.13	3.05	1.96
Metribuzin	Wlcorn	5.6	14	6.1	5.14	13	5.6	4.73	13	5.89	4.97
Metolachlor	GA peanuts	0.78	1.68	0.51	0.48	1.61	0.49	0.46	1.65	0.5	0.47
Norflurazon	FLCitrus	26	0.19	0.14	0.07	0.19	0.14	0.07	0.19	0.14	0.07
Thiamethoxam	Wlcorn	0.16	4.95	2.28	1.93	4.88	2.23	1.88	4.92	2.26	1.91
Sulfentrazone	NCCotton	37.4	9.97	2.9	2.77						

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## Appendix [SEQ Appendix \\* ALPHABETIC]. Summary of the Water Quality Portal Data Sources

The NAWQA program provides a nationally relevant dataset that includes analytes from a large list of pesticides and pesticide degradation products, larger than any other monitoring program of its scope and duration. However, the dataset is limited in that each of the 59 NAWQA Study Units (SU) have multiple objectives and are not specifically designed to evaluate the impacts of pesticide usage on drinking water supplies (*e.g.*, GW used as source drinking water) [ ADDIN EN.CITE

<EndNote><Cite><Author>Gilliom</Author><Year>2006</Year><RecNum>5350</RecNum><DisplayText><style face="superscript">79</style></DisplayText><record><rec-number>5350</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1585420662" guid="cd368b9-cd56-4b56-b0a4-dbfd22855992">5350</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>Gilliom, R.J.</author><author>Barbash, J.E.</author><author>Crawford, C.G.</author><author>Hamilton, P.A.</author><author>Martin, J.D.</author><author>Nakagaki, N.</author><author>Nowell, L.H.</author><author>Scott, J.C.</author><author>Stackelberg, P.E.</author><author>Thelin, G.P.</author><author>Wolock, D.M.</author></authors><secondary-authors><author>U.S. Geological Survey Circular 1291,</author></secondary-authors></contributors><titles><title>Pesticides in the Nation's Streams and Ground Water, 1992-2001</title><tertiary-title>U. S. Geological Survey</tertiary-title></titles><dates><year>2006</year></dates><urls><related-urls><url>https://pubs.usgs.gov/fs/2006/3028/</url></related-urls></urls></record></Cite></EndNote>] [ ADDIN EN.CITE <EndNote><Cite><Author>DeSimone</Author><Year>2009</Year><RecNum>5348</RecNum><DisplayText><style face="superscript">57, 80</style></DisplayText><record><rec-number>5348</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1585419485" guid="813a8c6a-f893-4221-b90a-2b936372bc09">5348</key></foreign-keys><ref-type name="EPA Document">51</ref-type><contributors><authors><author>DeSimone, J.L.</author><author>Hamilton, P.A.</author><author>Gilliom, R.J.</author></authors><secondary-authors><author>U.S. Geological Survey Circular 1332,</author></secondary-authors></contributors><titles><title>The quality of our Nation's waters—Quality of water from domestic wells in principal aquifers of the United States, 1991–2004—Overview of major findings</title><tertiary-title>U.S. Geological Survey</tertiary-title></titles><dates><year>2009</year></dates><urls><related-urls><url>https://pubs.usgs.gov/circ/circ1332/</url></related-urls></urls></record></Cite><Cite><Author>Toccalino</Author><Year>2014</Year><RecNum>5314</RecNum><record><rec-number>5314</rec-number><foreign-keys><key app="EN" db-id="s0xer2w2o0xwx3e0a0tx0sz3zradttw529er" timestamp="1584184602" guid="07061e8e-6ab9-4ac5-bc39-d33fe5b25213">5314</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Toccalino, Patricia L.</author><author>Gilliom, Robert J.</author><author>Lindsey, Bruce D.</author><author>Rupert, Michael G.</author></authors></contributors><titles><title>Pesticides in Groundwater of the United States: Decadal-Scale Changes, 1993–2011</title></titles><pages>112-125</pages><volume>52</volume><number>S1</number><dates><year>2014</year></dates><isbn>0017-467X</isbn><urls><related-urls><url>https://ngwa.onlinelibrary.wiley.com/doi/abs/10.1111/gwat.12176</url></related-urls></urls><electronic-resource-number>10.1111/gwat.12176</electronic-resource-number></record></Cite></EndNote>],19.

More than half of the NAWQA GW monitoring sites are used as domestic and public drinking water; however, this evaluation did not specifically distinguish between observed concentrations in drinking water supply wells versus other observation wells included in the

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<sup>19</sup> Gilliom *et al.* 2006 provides an overall perspective on the pesticide monitoring program. Domestic well water monitoring results are summarized in DeSimone *et al.* (2009) and public well water supply results are presented in Toccalino and Hopple (2010).



The NAWQA program has estimates of agricultural pesticide usage by crop and by state (and sometimes by county) over the course of the monitoring program; however, it is still not possible for this assessment to estimate usage in the zone of influence for each monitored well over the entire time scale that is relevant to the observed concentrations. Often pesticide usage for decades prior to the sampling date is needed to accurately associate usage of a specific pesticide with what might be observed in a GW sample. In addition, NAWQA well locations are diverse and include urban watersheds and other areas where few or no pesticides are used. While extensive, the NAWQA program does not encompass the entire United States, capture all agricultural areas, or capture all high pesticide use areas. Therefore, the observed concentrations may not represent the highest GW concentrations that could be observed for a particular pesticide.

The NAWQA program study units do not specifically target vulnerable GW supplies (*i.e.*, wells drawing from an unconfined high water-table aquifer in high pesticide use areas—similar to the conceptual model implemented in PRZM). In some study areas the aquifers sampled by NAWQA wells are deeper and more confined than in the conceptual model. Only a subset of the NAWQA measurements are from shallow, unconfined aquifers similar to the conceptual model. For example, 75% of the wells were drilled to a depth greater than 31 feet and, for sites with such information, 75% of the wells were screened starting at >20 feet below ground surface (bgs) and 50% at >50 feet bgs<sup>20</sup>. Ancillary data concerning well characteristics (*e.g.*, depth to GW) and GW properties are typically available for samples sites included in the NAWQA dataset, and these data could permit additional evaluation and characterization. However, this characterization was not completed.

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<sup>20</sup> Source: Download on 6/4/2012 of well site data from the NAWQA Data Warehouse at: [http://infotrek.er.usgs.gov/nawqa\\_queries/jsp/sitemaster.jsp](http://infotrek.er.usgs.gov/nawqa_queries/jsp/sitemaster.jsp). Well screening depths were recorded for 89% of the sites.

## Appendix [SEQ Appendix \\* ALPHABETIC]. Additional Information on the Comparison of Measured Concentrations from the Water Quality Portal to Model Estimated Concentrations

This Appendix summarizes the monitoring results for all samples available in the WQP (including dissolved, total, and recoverable) while **Section 6** focuses on the WQP results for dissolved fractions only.

**Table H1** summarizes the of the comparison of the PWC modeling to the WQP monitoring maximum concentrations of all sample fractions (dissolved, total, recoverable) for each pesticide. Results are summarized by changes in the ASM zone assumptions where the analysis covered 59 chemicals. Results are also summarized for chemicals that are stable to hydrolysis and where the assumption of 10x the ASM input was used for the hydrolysis input for 42 chemicals.

**Table H1. Comparison of the Peak Modeled Groundwater Concentrations to the Maximum Water Quality Portal Measured Concentration (All Samples)**

(b) Zone of Aerobic Soil Metabolism

Zone of ASM	Number of Pesticides (Percent of Pesticides); N=59 <sup>1</sup>				
	Equal to or Higher <sup>1</sup>	Total Lower	<10x Lower	10x to 100x Lower	>100 Lower
1m	44 (75%)	15 (25%)	8 (14%)	3 (5%)	4 (7%)
2m	40 (68%)	19 (32%)	8 (14%)	4 (7%)	7 (12%)
3m	37 (63%)	22 (37%)	9 (15%)	4 (7%)	9 (15%)
4m	36 (61%)	23 (39%)	9 (15%)	5 (8%)	9 (15%)

(c) Zone of Aerobic Soil Metabolism and Assuming the Hydrolysis Input is 10x ASM

Zone of ASM	Hydrolysis Assumption	Number of Pesticides (Percent of Pesticides); N=42 <sup>1</sup>				
		Equal to or Higher	Total Lower	<10x Lower	10x to 100x Lower	>100 Lower
1m	None	37 (88%)	5 (12%)	4 (10%)	0	1 (2%)
2m	None	34 (81%)	8 (19%)	5 (12%)	0	3 (7%)
3m	None	32 (76%)	10 (24%)	5 (12%)	2 (5%)	3 (7%)
4m	None	31 (74%)	11 (26%)	5 (12%)	3 (7%)	3 (7%)
1m	10x ASM	34 (81%)	8 (19%)	5 (12%)	2 (5%)	1 (2%)
2m	10x ASM	32 (76%)	10 (24%)	6 (14%)	1 (2%)	3 (7%)
3m	10x ASM	32 (76%)	10 (24%)	5 (12%)	2 (5%)	3 (7%)
4m	10x ASM	30 (71%)	12 (29%)	6 (14%)	3 (7%)	3 (7%)

<sup>1</sup> In this column the number of chemicals (percent of chemicals) analyzed where the PWC modeled concentration was 'equal to or higher' than the measured concentrations from the WCP, 'Lower', '<10x Lower', '10x-100x lower', or >100x lower than the maximum WQP measured concentration.

Overall, standard assumptions and the modified modeling have less than 7-15% of the modeled concentrations more than 100x lower than the WQP measured concentration and 5 to 8% of modeled concentrations between 10x to 100x lower than WQP measured concentrations. For

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all modeling assumptions modifications between 61 and 75% of modeled concentrations were equal to or higher than the WQP measured concentrations.

Increasing the zone of ASM degradation from 1 meter to 4 meters increases the number of chemicals that fall below the WQP measured concentration from

- 15 (25%) chemicals at 1m, to
- 19 (32%) chemicals at 2m, to
- 22 (37%) chemicals at 3m, and to
- 23 (39%) at 4m.

The 3m and 4m result are almost identical. The number of chemicals where the modeled concentration is more than 10x lower than the WQP measured concentration increases from 7 (12%) chemicals at 1m to 14 (24%) chemicals at 4m.

When examining how assuming a background degradation of 10x the ASM input for chemicals that are stable to hydrolysis, the baseline to compare to for the standard analysis includes only 42 chemicals that were stable to hydrolysis (**Table H1b**). In the standard assumptions for these 42 chemicals, 37 chemicals (88%) had results higher than the measured WQP concentration and 5 (12%) modeled concentrations lower than the WQP measured concentration. When a 10x ASM assumption is used as the hydrolysis input and the zone of degradation is 1m the number of chemicals that fall below the WQP measured concentration increases from

- 1 (2%) chemical at 1 m with no hydrolysis, to
- 3 (7%) at 1m with 10x ASM for hydrolysis, to
- 6 (14%) at 4m with 10x ASM for hydrolysis.

Most modeled concentrations that were lower than the WQP measured concentrations were within 10x lower than the WQP measured concentration.

In the **Figure H1**, the maximum measured WQP monitoring result is on the x-axis and the PWC modeled daily average concentration using different modeling assumptions is on the y-axis. When the modeled pesticide concentration exceeds the monitored concentration, the data point is above the 1 to 1 line, indicating that the modeled PWC EDWC is higher than the WQP measured concentration. When the monitoring concentrations are higher than the PWC modeled concentration, the datapoint is below the 1 to 1 line, indicating that the PWC modeled concentration was lower than the WQP measured concentration. These figures summarize the same data summarized in **Table H1**. Some of the predicted or measured concentrations were below 0.001 µg/L and are not shown in the figures.

When considering standard modeling (see the first panel in **Figure H1**), modeled concentrations exceeded the measured concentrations 75% of the time. Approximately 25% of maximum measured values were higher than the estimate from PWC standard modeling. Six pesticides had modeled concentrations more than 10x below the WQP measured concentrations (propanil, terbufos, azinphos-methyl, parathion-methyl, diazinon, malathion, and iprodione). Due to the persistence (short-half-life) and mobility (high Koc) of these pesticides, this is expected. The organic-carbon normalized distribution coefficients for these chemicals ranged from 8.4 to 1448 L/kg-oc and the soil-half-life used in modeling ranged from 0.5 to 123 days.

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When the zone of degradation is increased to 2 m, 3 m, or 4 m, three additional chemicals had modeled concentrations more than 10x below the WQP measured concentrations (2,4-D, aldicarb, and carbofuran).

When considering a background degradation rate for chemicals that do not undergo hydrolysis (**Figure H2**), the comparison to monitoring data is relatively similar whether the model simulations assumes a 10x or 25x the ASM rate. Therefore, the summary focused on the results assuming hydrolysis is 10x the ASM half-life for chemicals that are stable to hydrolysis. Propanil is the only chemical with modeled concentrations that were more than 10x below the WQP measured concentrations when considering only pesticides stable to hydrolysis and the 1m0x assumption<sup>21</sup>. When assuming 10x the ASM input for hydrolysis, two additional chemicals (2,4-D, aldicarb) had modeled concentrations more than 10x lower than the measured concentration, regardless of the zone of degradation assumed.

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<sup>21</sup> Terbufos, azinphos-methyl, parathion-methyl, diazinon, malathion, and iprodione are not stable to hydrolysis.

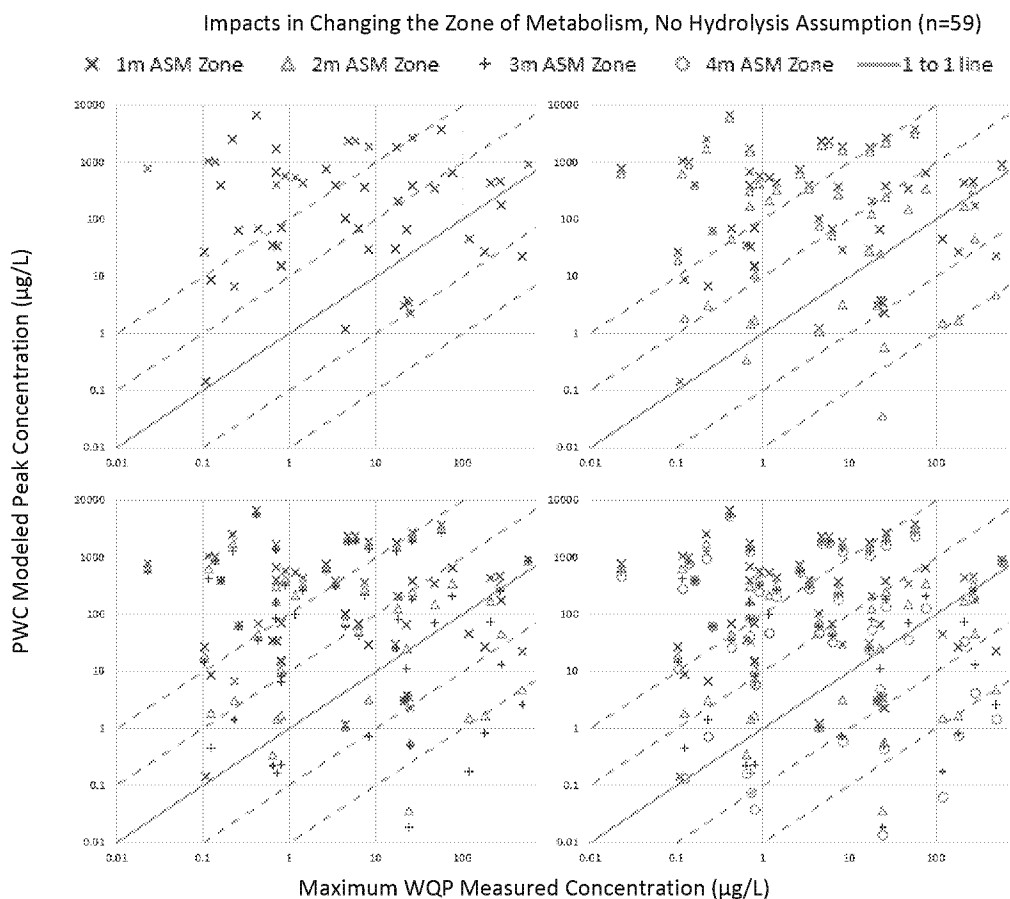


Figure H1. PWC Modeled Peak EDWCs Versus Maximum WQP Concentration (All Samples) – Hydrolysis Based on Data

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Impacts of Changing the Zone of Metabolism with Hydrolysis Half-life Assumed to be 10x ASM (n=42)

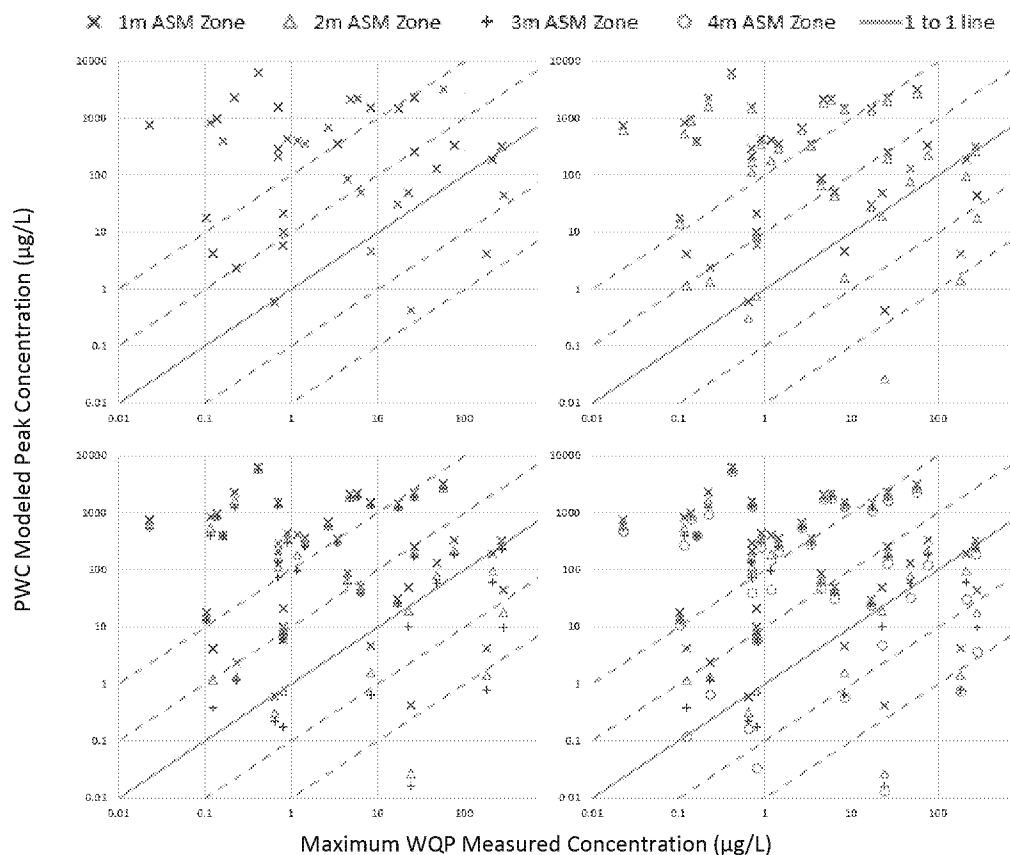


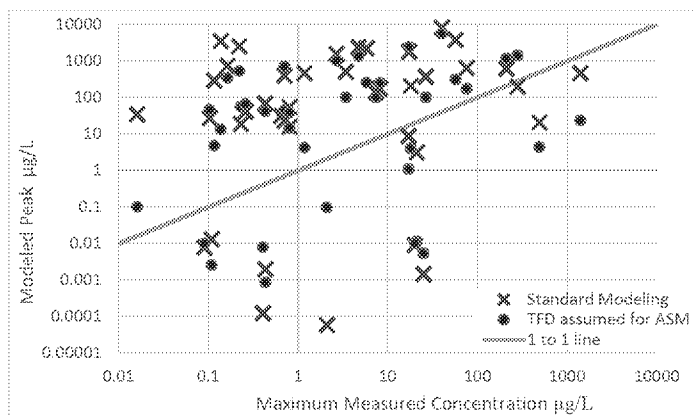
Figure H2. PWC Modeled Peak EDWCs Versus Maximum WQP Concentration (All Samples) – Hydrolysis Assumed 10x ASM

## Appendix [ SEQ Appendix \\* ALPHABETIC ]. Analysis of Using the Terrestrial Field Dissipation Half-life as the Aerobic Soil Metabolism Half-life Input in PWC Groundwater Modeling

The terrestrial field dissipation half-life was assessed as a potential refinement option. The main concern with this strategy is that the field dissipation studies simulate multiple mechanisms of loss, including leaching, which is simulated separately from ASM in the PWC modeling. In the PWC model, the ASM half-life is supposed to simulate only loss through aerobic soil degradation. So, if you use the terrestrial field dissipation half-life as the input, you could be potentially double count loss.

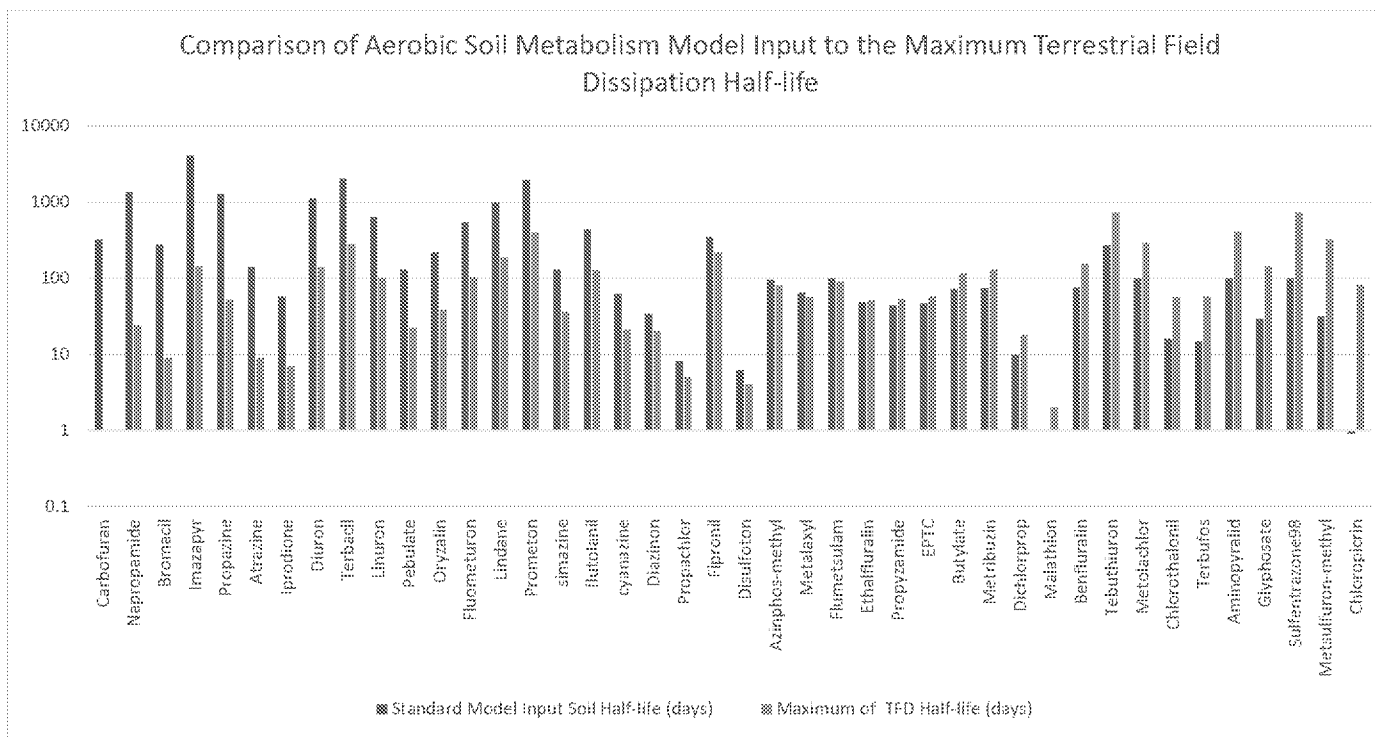
It was anticipated that the terrestrial field dissipation half-lives would most often be faster than the ASM input with the potential for double counting loss via other mechanisms other than ASM; therefore, the maximum terrestrial field dissipation half-life was used as the ASM half-life when the terrestrial field dissipation data were readily available.

Contrary to what was anticipated, in 41% of 42 chemicals, the terrestrial field dissipation half-lives were often longer than the ASM half-life; though the range generally included the values of the ASM half-lives (**Figure 12**). This illustrates 1) that the standard ASM half-life is not necessarily always conservative and 2) often is within the range of what is observed in the field. This also illustrates that both the ASM studies and field dissipation studies are important lines of evidence in understanding the fate of chemicals in the environment. In **Figure 11**, 12 datapoints are below the 1 to 1 line using the standard ASM model input and 11 (26%) datapoints are below the 1 to 1 line using the maximum terrestrial field dissipation half-life as the ASM PWC model input.



**Figure I1. Comparison of the Modeled Peak Pesticide Concentration in Groundwater Assuming the Standard ASM Input Versus Assuming the Maximum Measured Terrestrial Field Dissipation Half-life as the ASM Input in PWC Modeling.**





**Figure I2. Comparison of Standard Aerobic Soil Metabolism Model Input to the Maximum Terrestrial Field Dissipation Half-life**

## Appendix [SEQ Appendix \\* ALPHABETIC]. Analysis of Assuming a Measured Subsurface Metabolism Half-life as the Hydrolysis Half-life

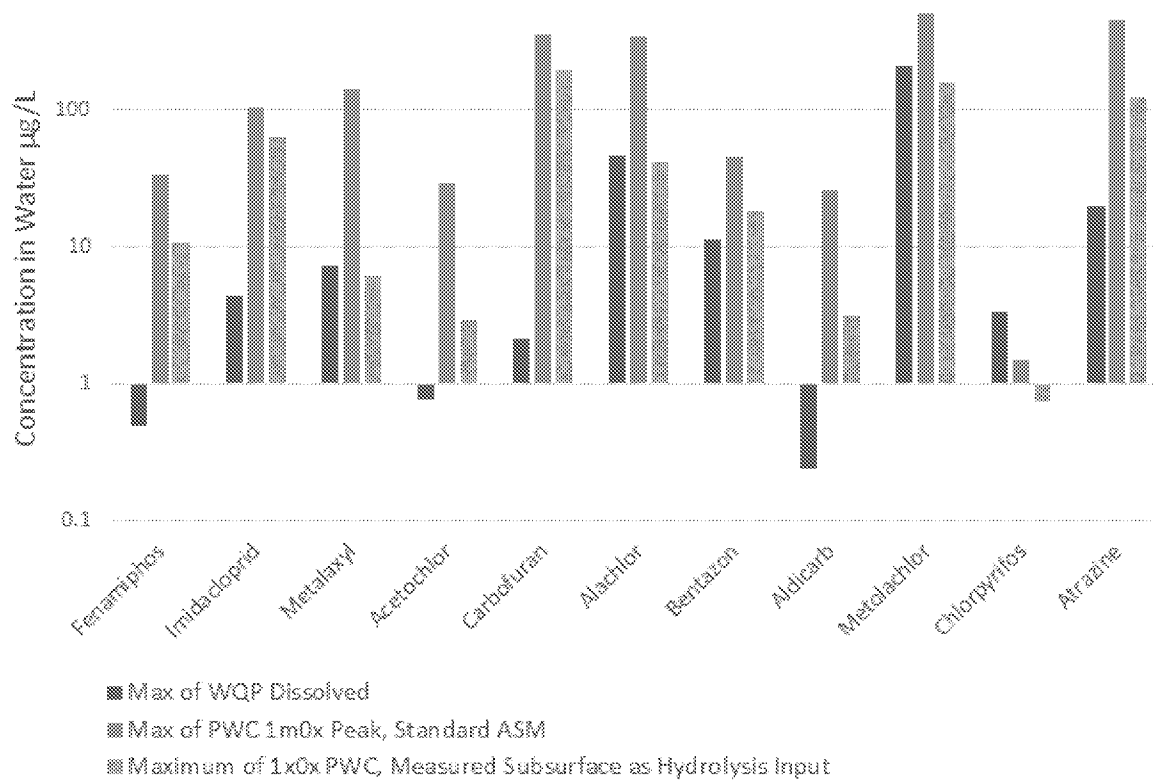
In order to evaluate how using a measured subsurface metabolism half-life in modeling would impact the modeling result, modeling was completed for chemicals where measured subsurface metabolism half-life values were available. The modeling was completed when the following conditions applied to the chemical:

- Monitoring data was available
- The measured subsurface metabolism half-life was slower than the ASM input but faster than the hydrolysis half-life

When multiple measured subsurface half-life values were available the maximum half-life was used as the hydrolysis half-life. Results of this effort are summarized in **Figure J1**.

Overall, assuming the subsurface metabolism half-life as the input for hydrolysis resulted in predicted concentrations that were higher than or within 25% of the maximum measured concentrations. All of the standard PWC modeled peak concentrations were higher than the maximum WQP pesticide concentration in GW (considering the dissolved fraction samples only). The ratio of the PWC modeled concentration using the measured subsurface half-life instead of the hydrolysis half-life were all greater than one (ranged from 0.22 to 21), except for four simulations. Three of the underpredicted concentrations were within 25% of the maximum measured concentration. The final underpredicted concentration occurred for chlorpyrifos, which was substantially underpredicted by 78%; however, the simulation did not have throughputs greater than one and is expected to result in underpredictions of potential exposure.

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**Figure J1. Comparison of Peak Groundwater PWC EDWC Using a Measured Subsurface Metabolism Half-life as the Hydrolysis Input to Maximum Dissolved Pesticide Concentration in Groundwater Reported by the Water Quality Portal**

Appendix [ SEQ Appendix \\* ALPHABETIC ], Comparison of EDWCs With Different Modeling Assumptions to Standard PWC EDWCs for the Water Quality Portal and Prospective Groundwater Data Sets

**Figure K1** compares measured GW concentrations for both PGW (red circles) and WQP (blue x's) pesticides based on modeling modifications to subsurface ASM depth with the impact of shallower to deeper depth changes arranged left to right, respectively (starting with no change from the standard 1m depth assumption and proceeding to a change in depth to 2, 3, or 4m). Similarly, modeling involving substitution of a fraction of the ASM rate as the hydrolysis input are compared to standard modeling vertically with no change from standard model assumptions at the top to substituting 25× the ASM half-life (*i.e.*, 1/25<sup>th</sup> the ASM rate) in the middle to substituting 10× the ASM half-life (*i.e.*, 1/10<sup>th</sup> the ASM rate) at the bottom. All combinations of model modifications to the ASM depth and substitution of the hydrolysis input are depicted in the graph. For example, combining an extension of the ASM depth to 4m with substituting 10× the ASM for the hydrolysis input is depicted in the lowest right-most graph of this figure.

EDWCs available from 10 PGW and 59 WQP pesticides. The graphs across the top of Figure H1 include 2 additional PGW and 17 additional WQP pesticides for which non-stable pH 7 hydrolysis values were available. (These pesticides were excluded from subsequent rows because of uncertainty in how to substitute a fraction of the ASM rate into the hydrolysis input when there was already a measured non-stable input.) The graph in the upper left-most corner is unimportant, since it is simply comparing the standard EDWCs (no change in ASM depth or hydrolysis input) to the standard EDWCs (*i.e.*, standard EDWCs vs. standard EDWCs); therefore, all the EDWCs unsurprisingly fall on the one-to-one line (perfect agreement). Note, that the range of EDWCs is much greater for the WQP pesticides than the PGW pesticides.

PWC EDWCs vary in a direct linear fashion with some parameters. For example, reducing the application rate by ½ will result in ½ the EDWC if no other model inputs are changed. In contrast, altering the depth to which ASM occurs or substituting a fraction of the ASM rate for the hydrolysis input changes EDWCs in a highly nonlinear fashion.

Considering only changes to the ASM depth (2<sup>nd</sup>, 3<sup>rd</sup>, or 4<sup>th</sup> graphs from the left in the top row of **Figure K1**), there are many pesticides that fall on or near the one-to-one line. Pesticides that do not move off the one-to-one line in these graphs are stable to ASM (*i.e.*, increasing the depth to which ASM occurs did not change EDWCs from the unrefined EDWCs, therefore these chemical's ASM rates are stable). Pesticides that remain close to the one-to-one line have slow rates of ASM (long half-lives) since doubling to quadrupling the ASM depth had relatively limited impact. Whereas, those chemicals that show a greater decrease in EDWCs (some with a >1000-fold decrease) have faster ASM rates (shorter half-lives).

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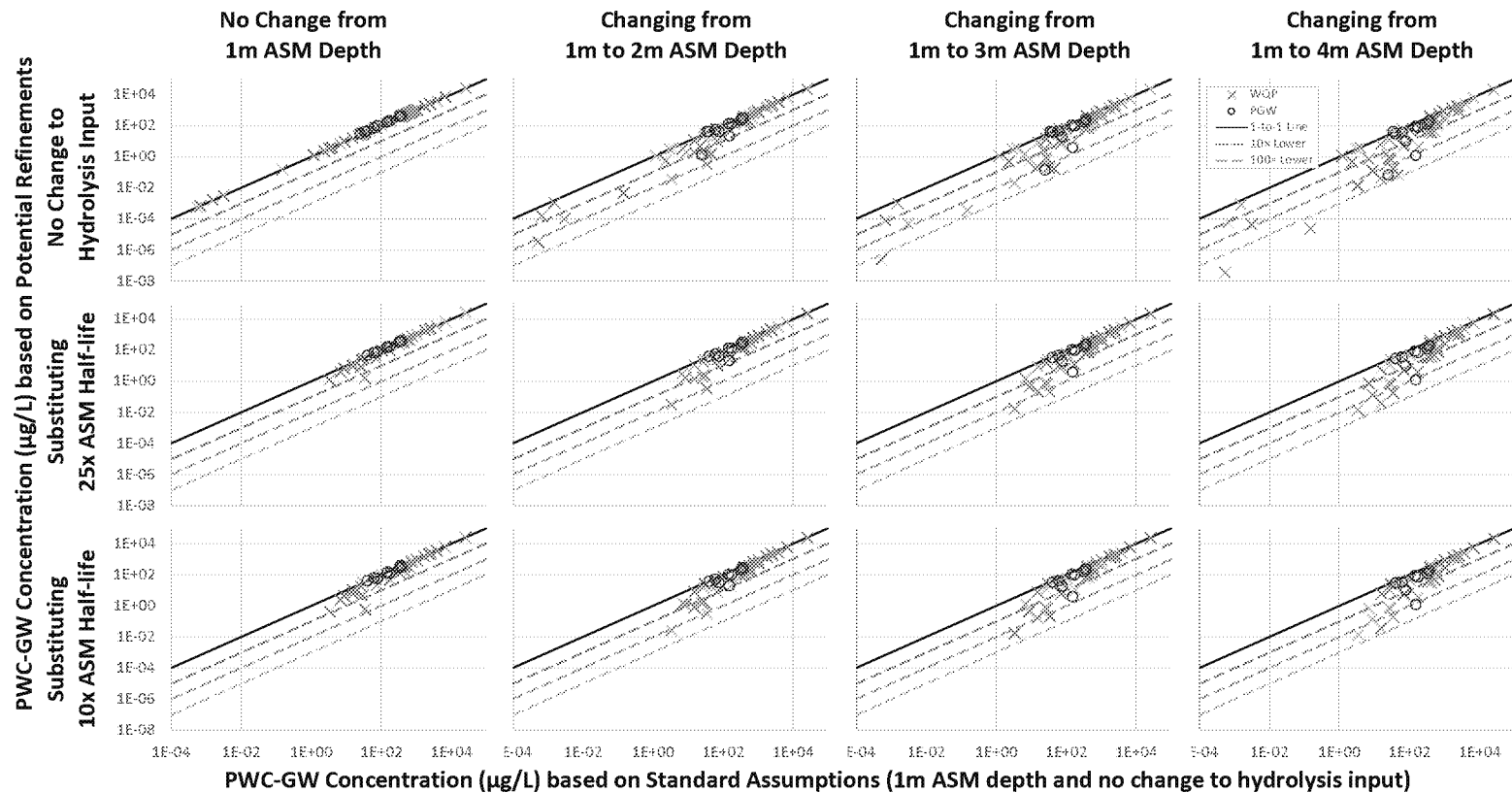


Figure K1. Comparison of 1-day Average Potential Refinement EECs to Standard PWC-GW EECs for the Water Quality Portal (WQP; blue x's) and Prospective Groundwater (PGW; red circles) Data Sets.

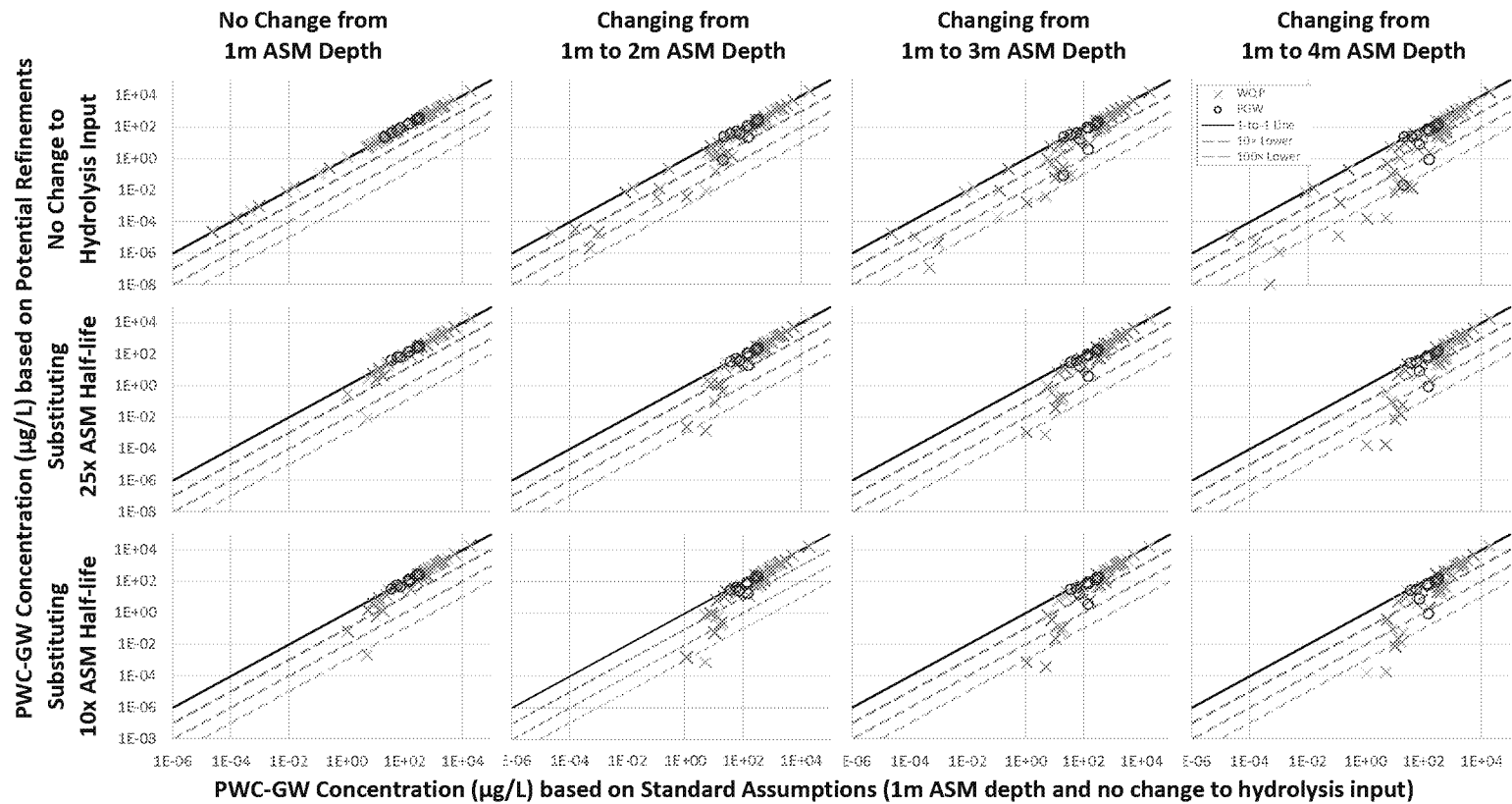
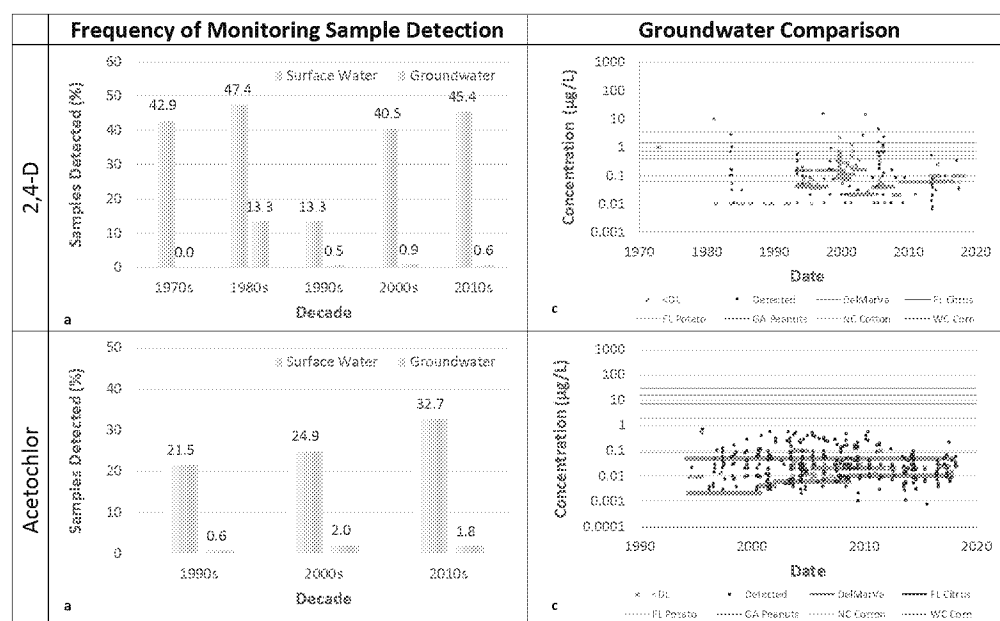


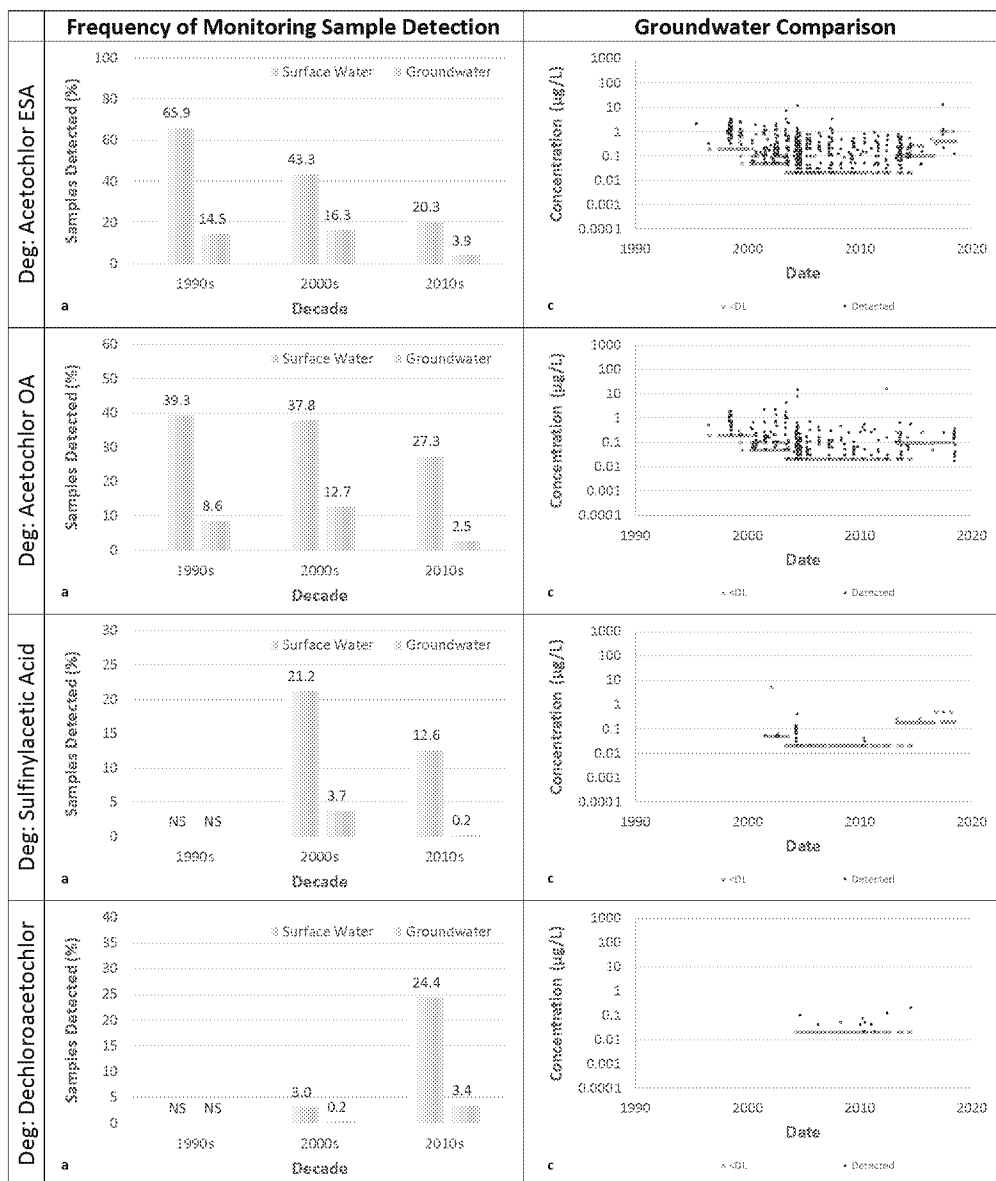
Figure K2. Comparison of Post-breakthrough Average Potential Refinement EECs to Standard PWC-GW EECs for the Water Quality Portal (WQP; blue x's) and Prospective Groundwater (PGW; red circles) Data Sets.

# Appendix [SEQ Appendix \\* ALPHABETIC]. Comparison of Modeled Peak Concentrations to Dissolved Phase Monitoring Concentrations for Groundwater by Pesticide

The following graphs allow a better understanding of the detection frequency, how many detections occur in different concentration ranges, and when those detections were occurring. The first graph displays the frequency of detection frequency for different decades. The second graph panel displays the detection limit (DL) of each sample collected without a detection, detections in red, over time. The graphs also provide an analysis of the PWC predicted groundwater concentrations for different scenarios. As an example, for 2,4-D there were three detections above PWC estimated concentrations in groundwater, but most detections were within the predicted range or lower. For acetochlor, all detections were below the concentrations predicted in groundwater using PWC groundwater modeling.

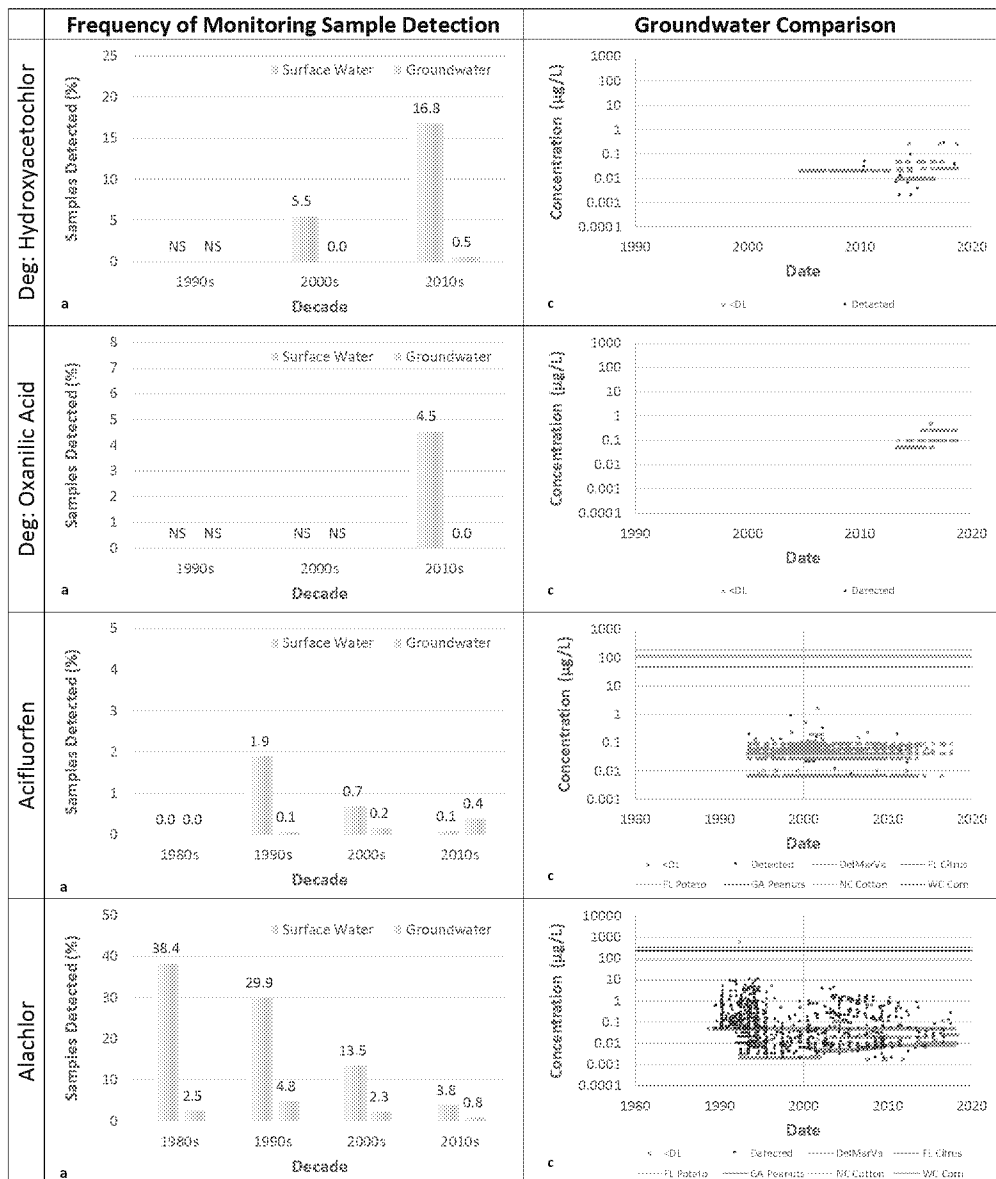


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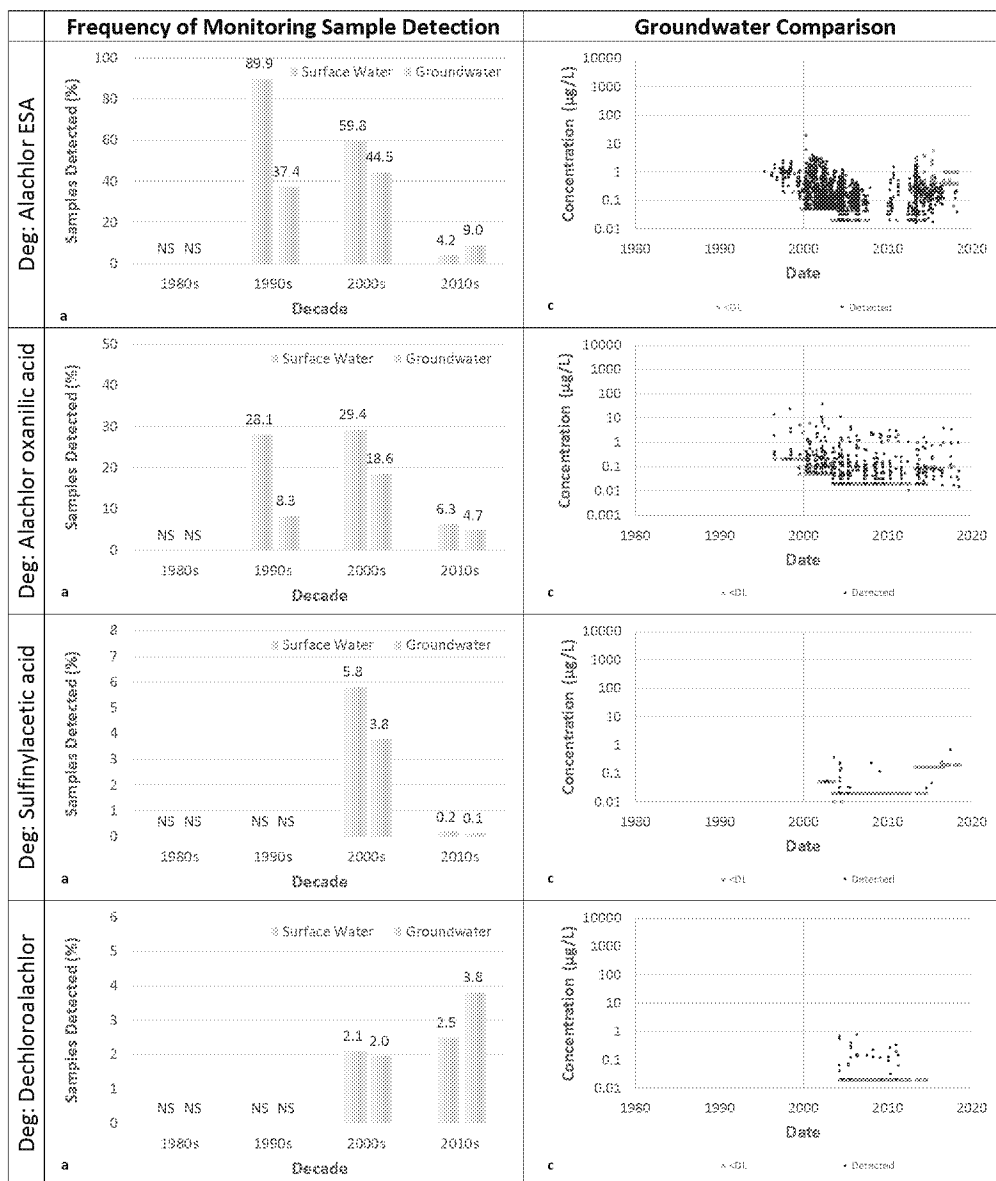


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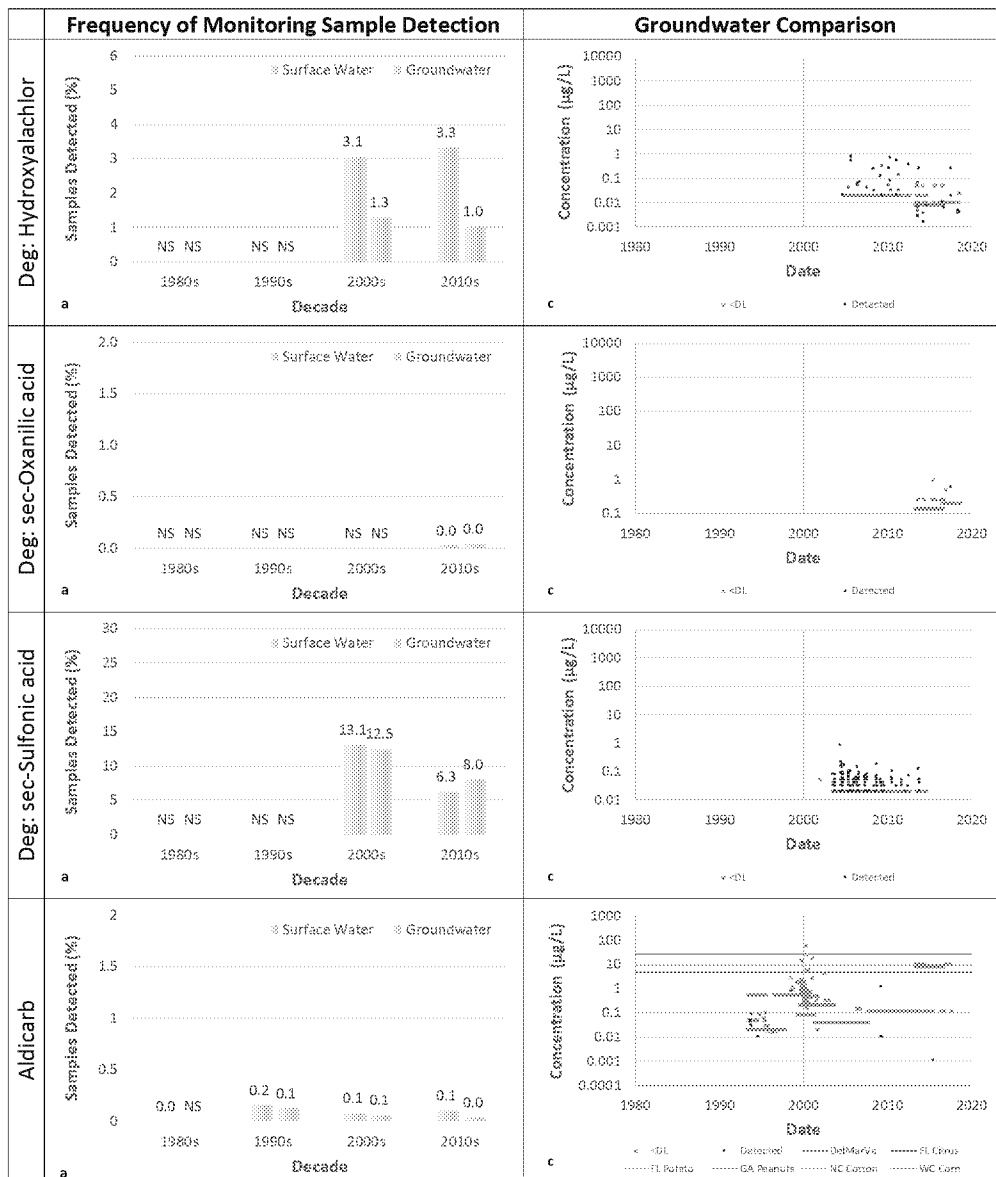




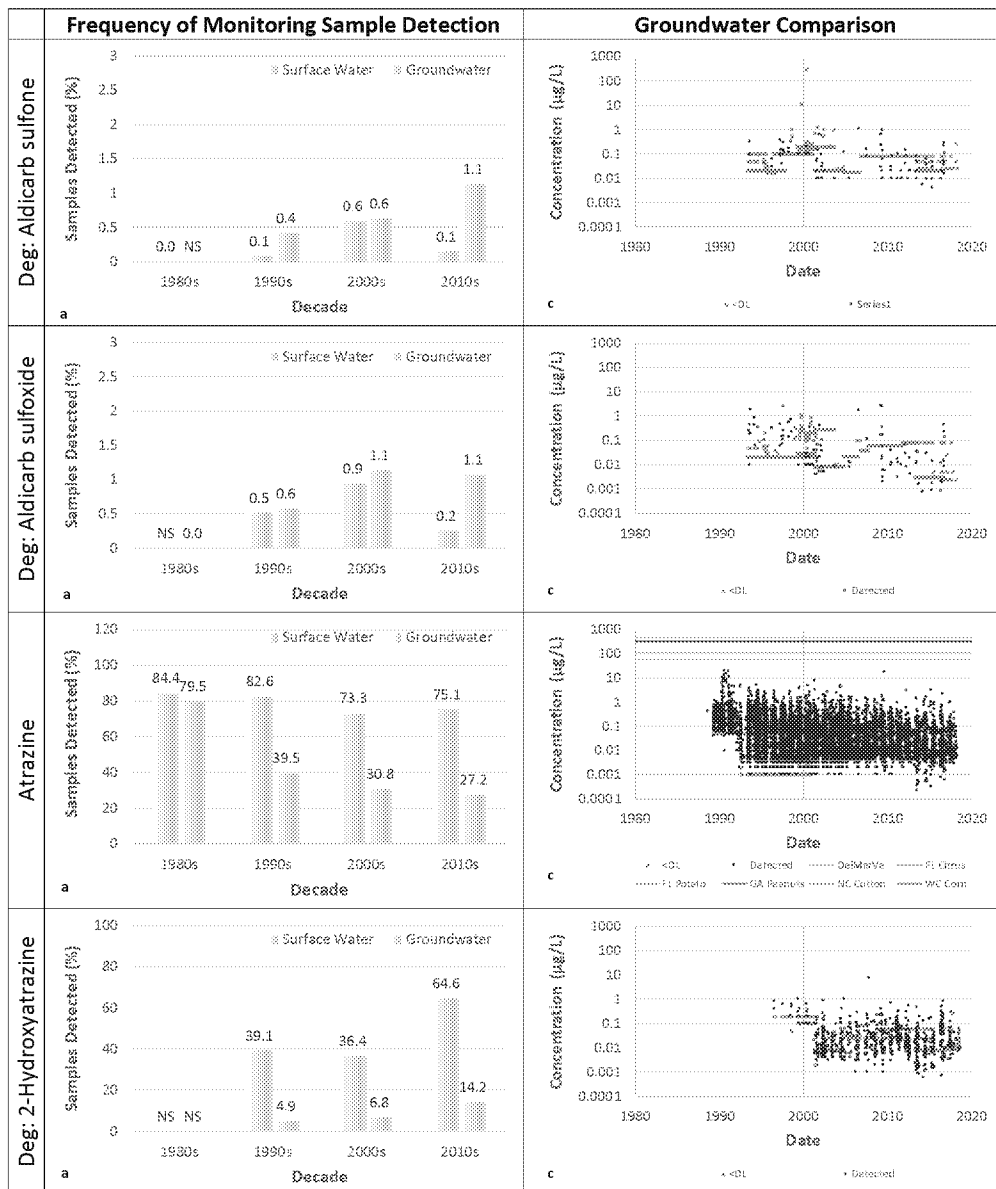
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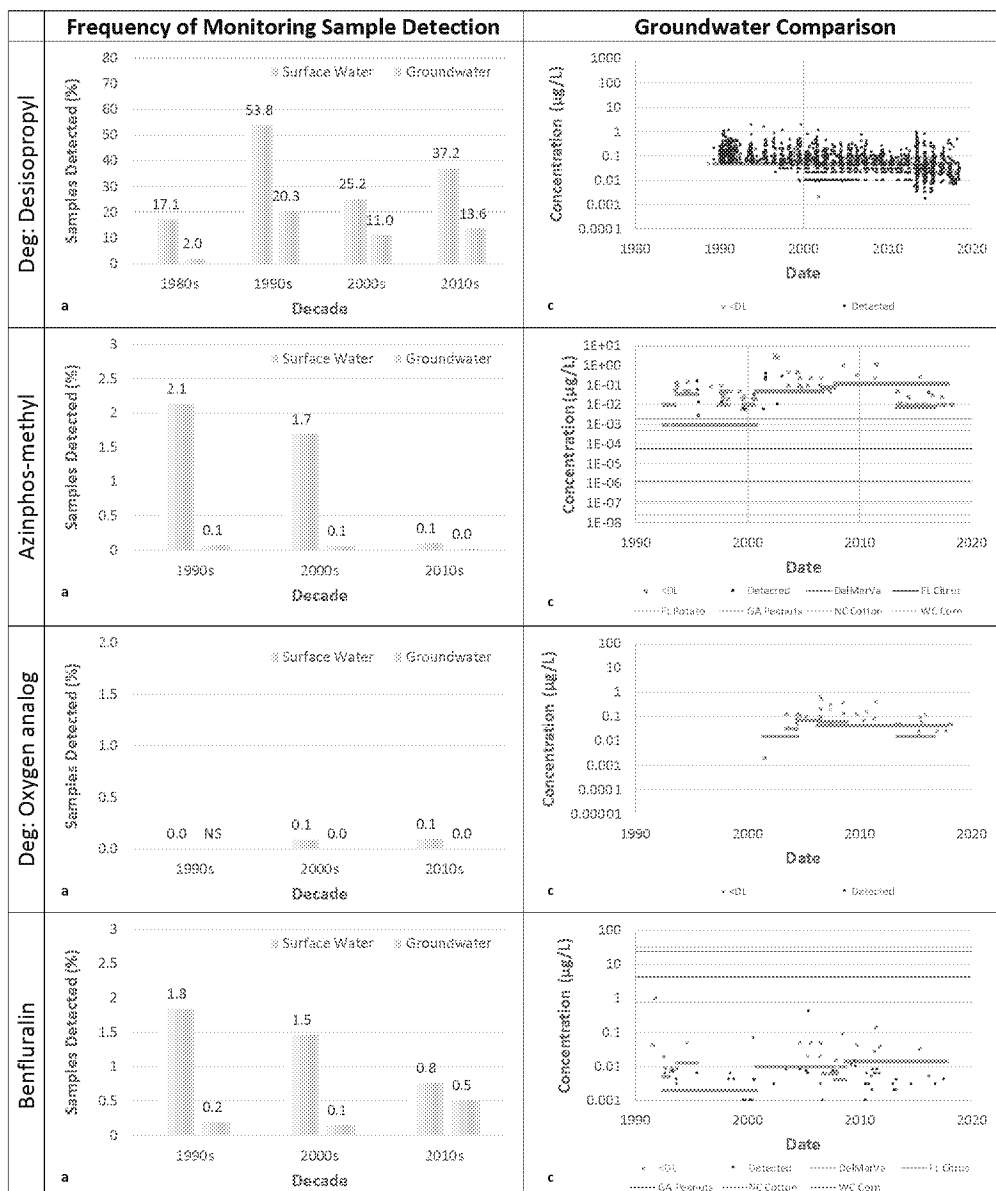
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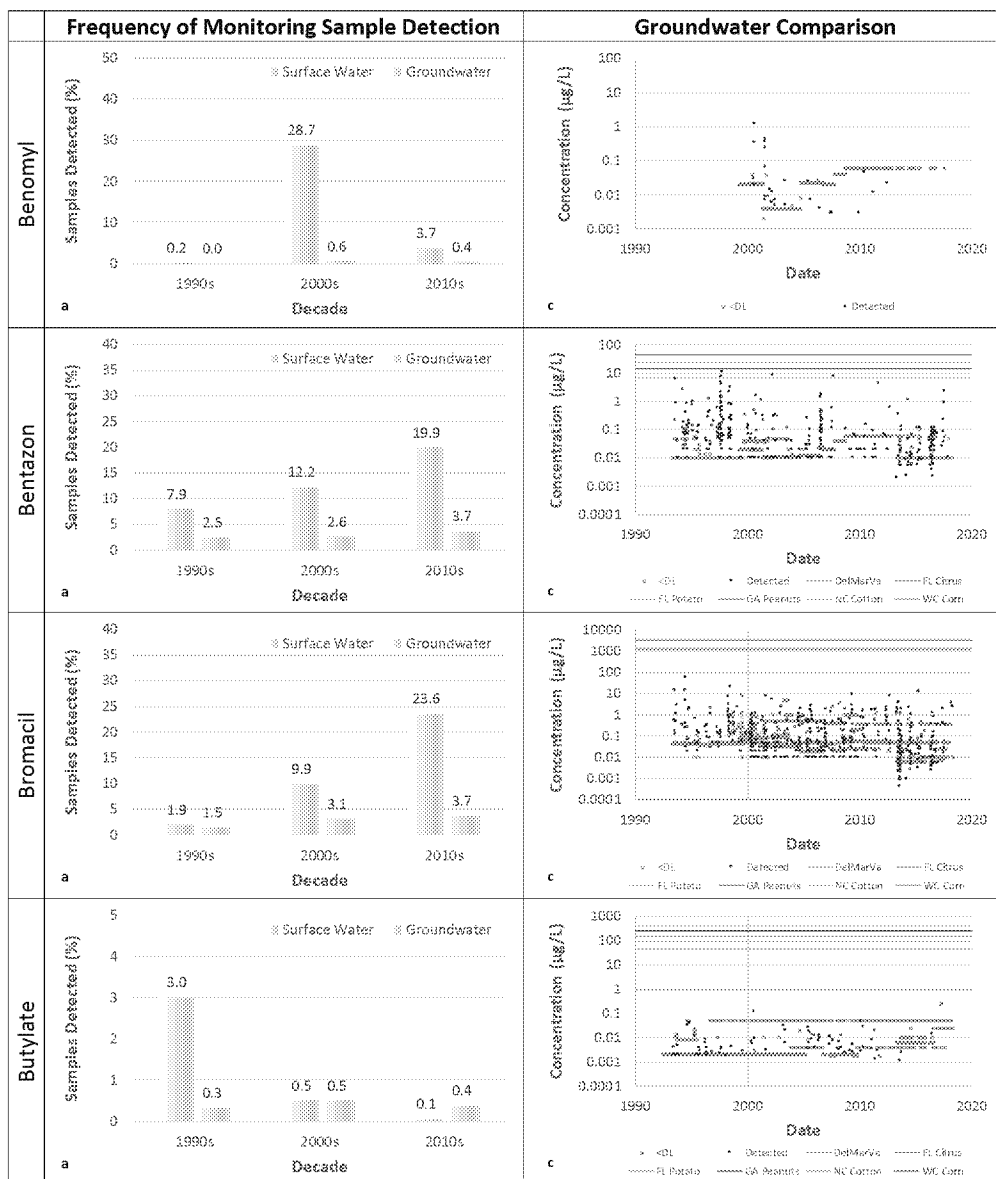
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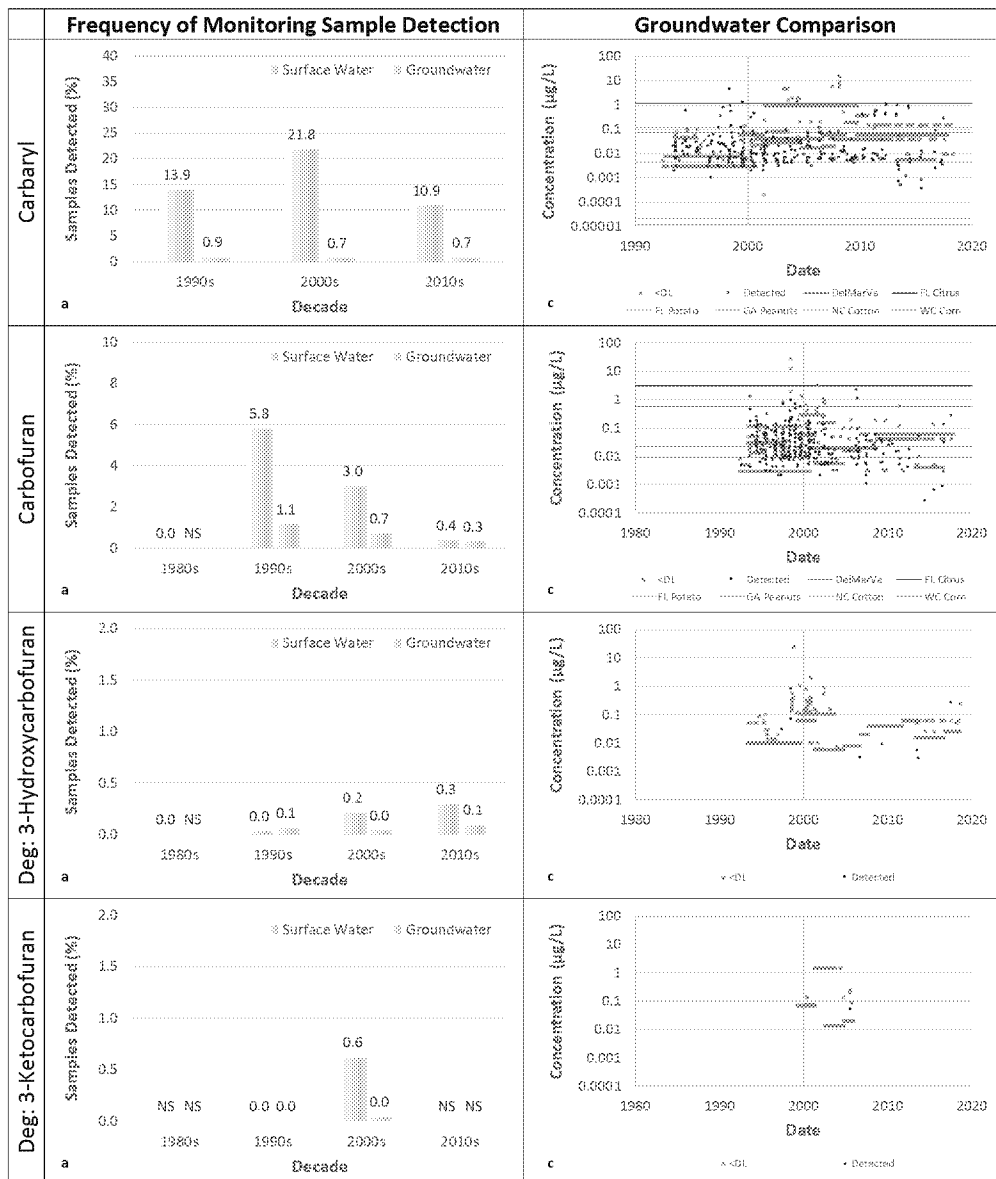
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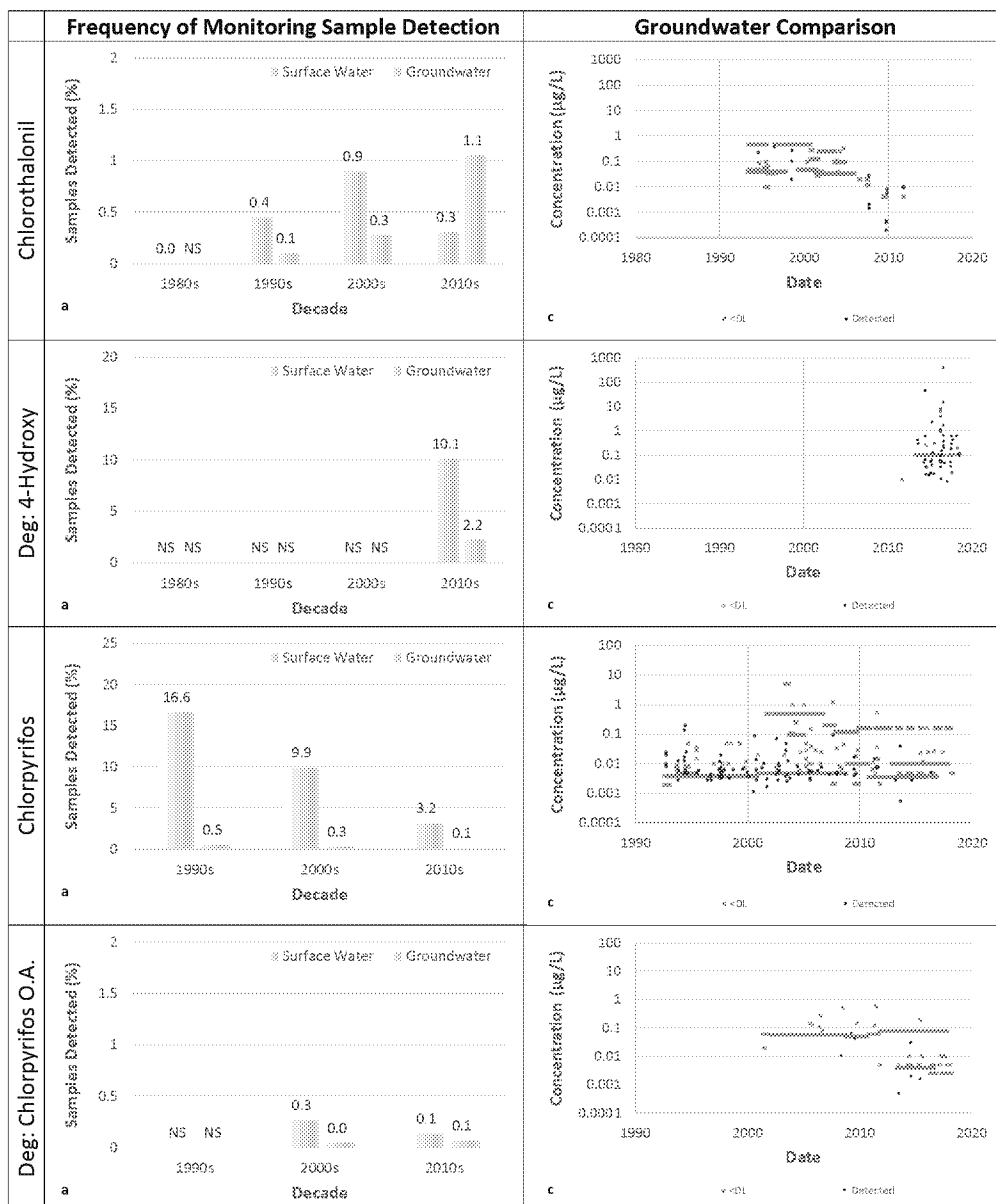
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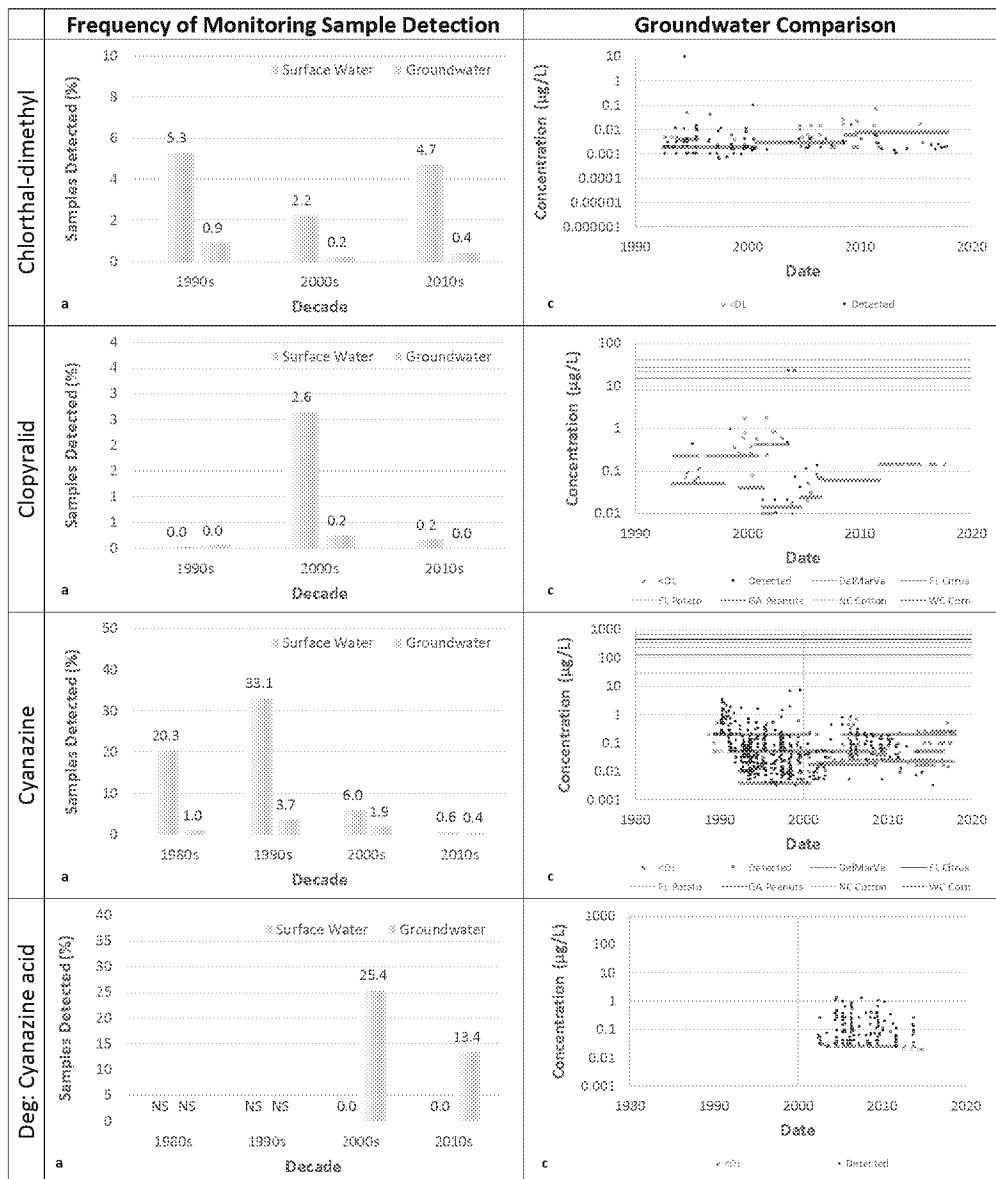


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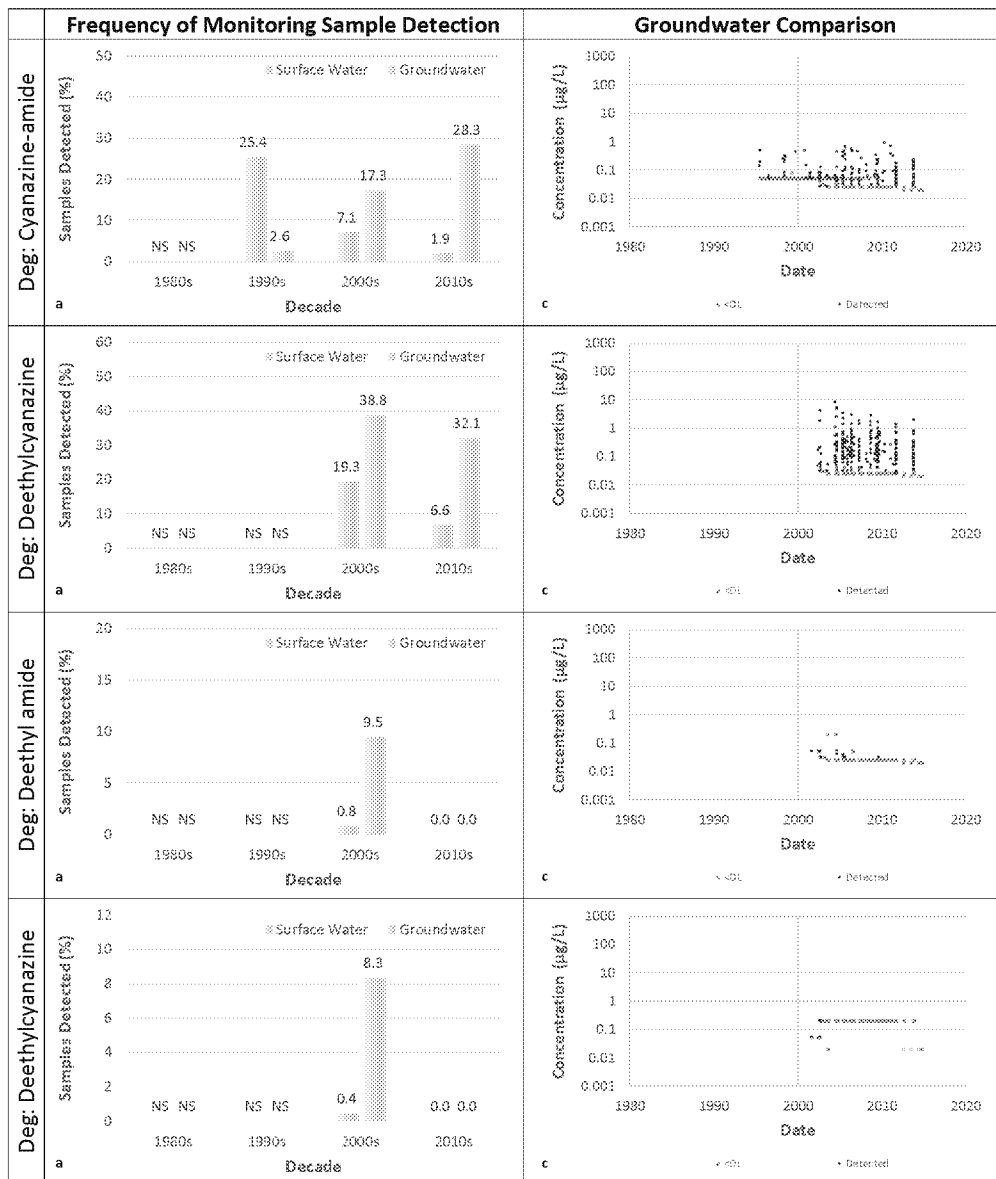


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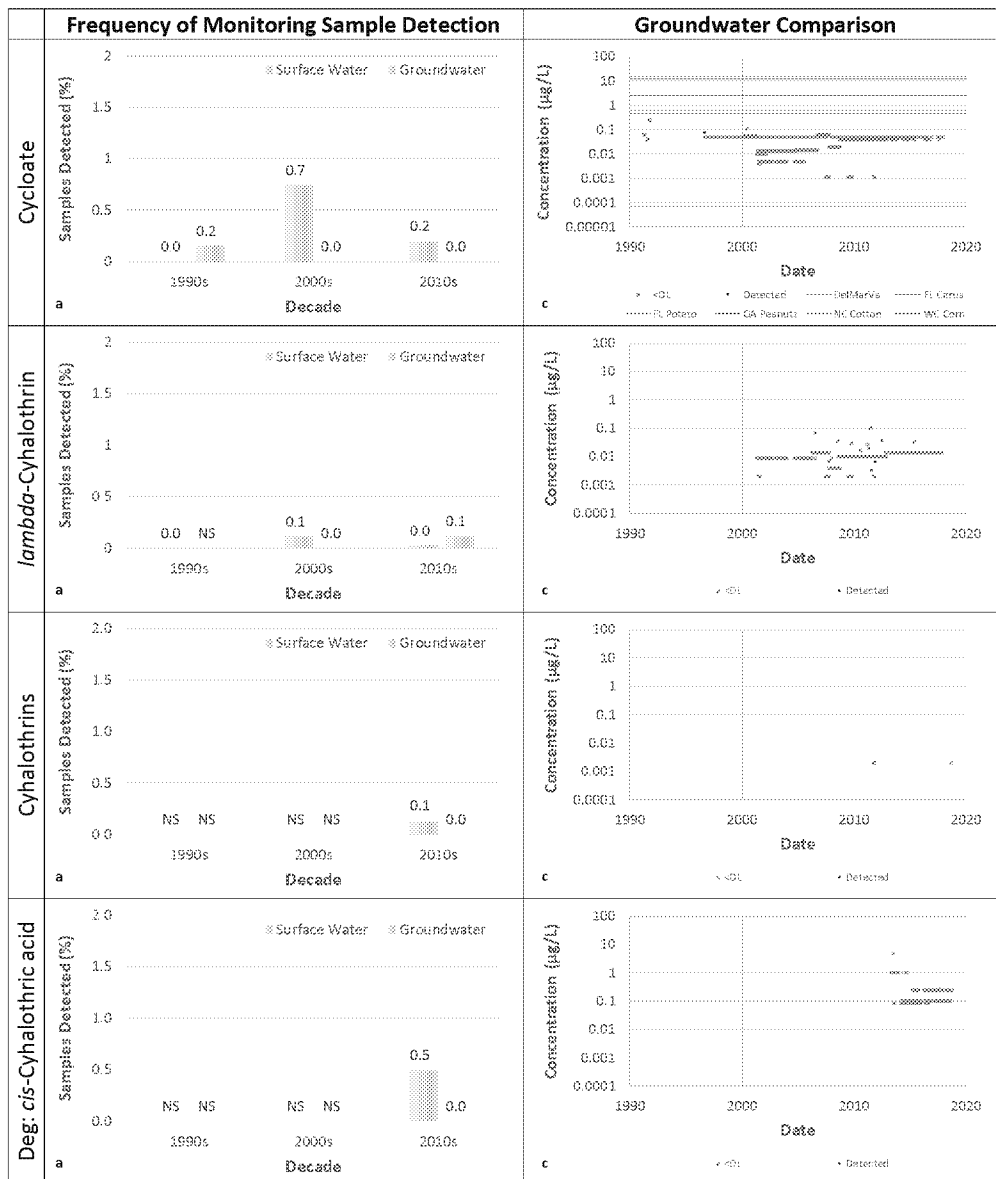




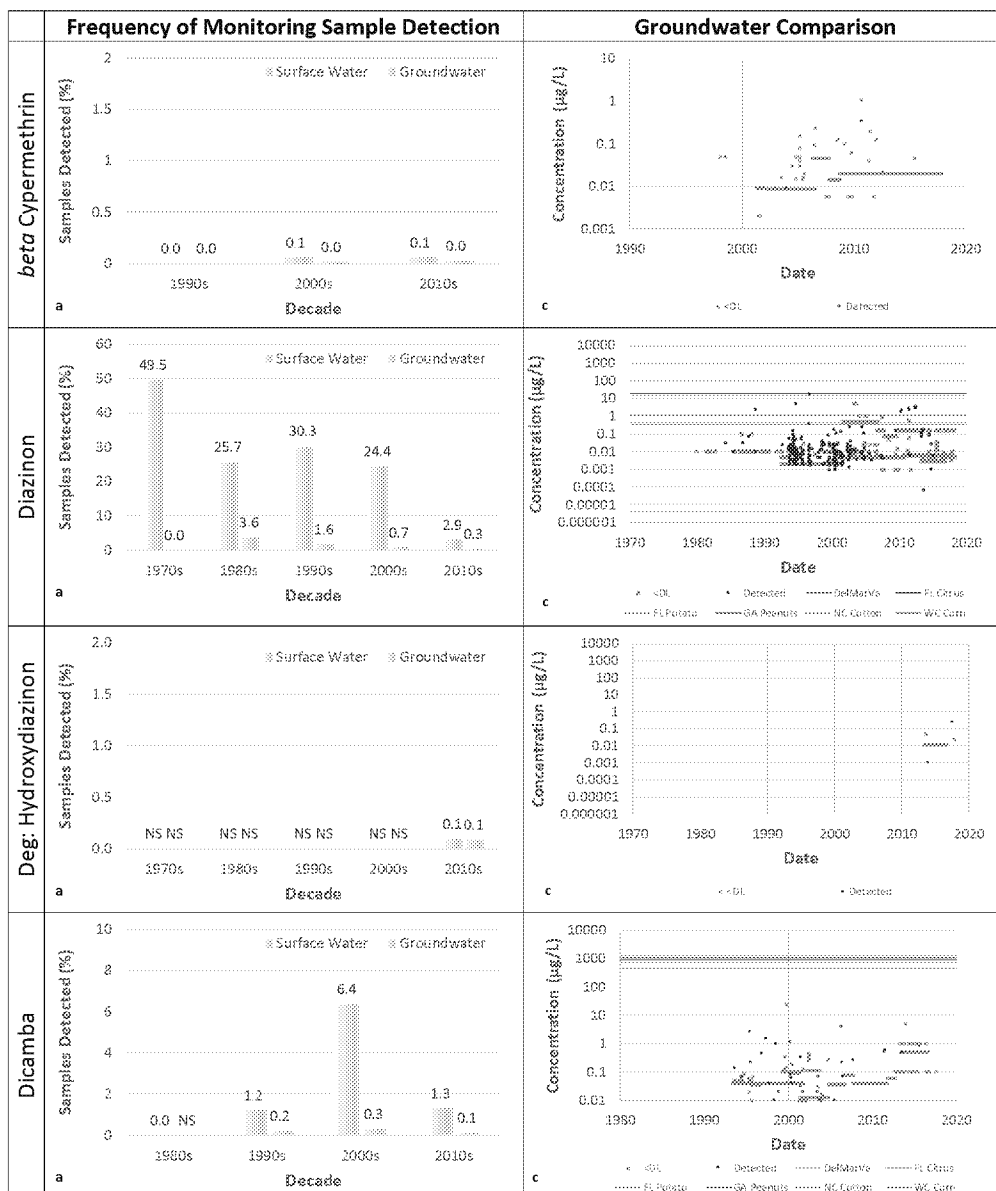
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